Atmospheric Ammonia:

Emission, Deposition and Environmental Impacts. Poster Proceedings.

Poster papers and abstracts from the
International Conference on Atmospheric Ammonia.
Culham, Oxford 2-4 October 1995

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Edited by: M.A. Sutton, D.S. Lee, G.J. Dollard and D. Fowler

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Forward

The International Conference on Atmospheric Ammonia was organized with the intention to provide a wide ranging overview of the current scientific understanding of NH_3 in the atmosphere and its effects on the terrestrial environment. Interest in NH_3 has increased substantially over recent years, both in relation to the role of NH_3 as a base in atmospheric chemistry and its contribution to acidification and nitrogen deposition effects on ecosystems. The conference considered the full atmospheric cycle from emission, atmospheric chemistry and modelling, biosphere-atmosphere exchange, the cycling of nitrogen at the ecosystem level as well as physiological and ecological impacts, concluding with a discussion on control policies. Over 40 oral and 50 poster presentations were given at the conference which attracted over 150 attendees.

The proceedings of the conference have been published in two parts. A special issue of the journal *Atmospheric Environment* contains peer-reviewed papers from the oral programme and selected posters. The present volume reports the results from the large number of posters presented at the meeting, it also contains additional abstracts for other presented talks and posters, as well as the participants list of the conference.

The conference was sponsored by the United Kingdom Department of the Environment, with the central focus being the quantification of fluxes and impacts, which is necessary to underpin understanding and development of control policy for NH_3. Present developments within the UNECE on a new NO_x or Nitrogen Protocol are considering controls of NH_3 in relation to the critical loads approach. This demands a sound knowledge of the atmospheric cycle, impacts and potential for controls.

The sessions demonstrated the high level of research activity on quantification of emissions, illustrated by the number of posters presented. This includes work on developing the sampling methodology needed to quantify emissions, measurements and modelling of the process interactions governing emissions, and scaling-up activities considering the temporal trends of regional ammonia emissions and their spatial distribution. Substantial progress has been made in improving the basis for quantifying NH_3 emissions in N.W. Europe, though estimates are still very uncertain. The development of analytical techniques, in particular annular denuders, has enabled rapid progress in monitoring, understanding atmospheric chemistry and measuring surface-atmosphere exchange.

The current development of atmospheric modelling of NH_3 was considered at a range of scales from global and hemispheric to national and local scale studies. Although NH_3 is transported over long distances, a key aspect is its local variability and studies are only now beginning to address this variability in relation to critical loads and impacts. A series of papers reported progress in quantifying biosphere-atmosphere exchange fluxes of NH_3. The bi-directional nature of NH_3 fluxes substantially complicates the issue, and although there are now some long-term site specific measurements of NH_3 fluxes, there is still debate over modelling the exchange process and the importance of gas-particle reactions.

In recognizing the importance of the biological role of NH_3, two sessions were devoted to ecosystem cycling of NH_3 and impacts studies. Key progress was shown in the development of a physiological basis for plant-atmosphere NH_3 exchange, which will greatly aid the development of biosphere-atmosphere exchange models. Other work investigated the link between NH_3 and SO_2 fluxes, showing controlled release of NH_3 to enhance SO_2 deposition rates. Impacts of ammonia were considered at both plant physiological and ecosystem levels, including the effects on leaf acid-balance, woodland ground flora, lichens and forests, as well as on atmospheric CH_4 consumption and N_2O emission by forest ecosystems. Athough clear effects on ground flora, wetland ecosystems, CH_4 and N_2O fluxes were reported, the role of NH_3 on the productivity and decline of amenity or production forest remains uncertain.

The final session considered the development of work in the UNECE on the new Nitrogen Protocol, together with papers on the economic costs and potential for NH_3 emissions reductions. A key finding is that some reductions in NH_3 emissions may be cheaper than NO_x emissions, but that the percentage reductions possible (20-60%) are likely to vary greatly for different countries in relation to agricultural practice. The final oral presentation considered the potential consequences for agriculture of NH_3 controls, using recent experience from the Netherlands as a basis for the assessment. The large potential economic and social costs, shown in relation to Dutch NH_3 policy, demonstrate the need for a better scientific understanding of the behaviour of atmospheric ammonia to underpin the control policy.

The organisers are grateful to the Department of the Environment and all participants for their valuable contributions to the Conference, especially those presenting posters and papers, as well as those refereeing papers. Particular thanks are due to the organising secretariat, Sarah Espenhahn, Marjorie Ferguson and Carole Pitcairn.

M.A. Sutton, D.S. Lee, G.J. Dollard and D. Fowler

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A METHOD FOR IN SITU MEASUREMENT OF AMMONIA EMISSIONS FROM ORGANIC FERTILIZERS IN PLOT EXPERIMENTS

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Abstract–Accurate measurement of NH_3 volatilization is required to test strategies reducing NH_3 emission from organic fertilizers. In plot experiments the wind tunnel method is frequently used to quantify NH_3 volatilization. This method, however, is expensive and alters climatic parameters (e.g. precipitation, wind rose). We developed a new method to measure NH_3 volatilization under ambient climatic conditions (including rain and wind) on small experimental plots (e.g. 2 x 5 m). Being technically simple and cheap, the method can be used on bare or cropped soils with no restriction on plot number. The method is based on an indirect measurement by comparing NH_3 volatilization from sources of unknown to NH_3 volatilization from sources of known strength. In addition to manured plots, standard plots artificially releasing known rates of NH_3 via a tubing system are installed. Each plot is equipped with a passive sampler collecting NH_3 in sulfuric acid. Ammonia concentrations in the samplers of fertilized plots are compared to those of standard plots. Provided that wind conditions are homogeneous throughout the experimentation site, NH_4^+ concentration of samplers is a linear function of NH_3 source strength. Thus, NH_3 volatilization from manured plots can be calculated from collected NH_3 and known source strength of standard plots. The functioning of this method is illustrated by a study on NH_3 volatilization along with slurry application.

Key word index: Ammonia, volatilization, measurement technique, slurry.

INTRODUCTION

Ammonia volatilization from animal wastes, especially slurry, contributes to hazardous atmospheric N inputs into near-natural ecosystems (Asman and Jaarsveld, 1992; Ellenberg, 1992). When applied to land, plant available N content of slurry is decreased by NH_3 losses, making it difficult to assess its effects on plant production and diminishing its fertilizer value (Panse *et al.*, 1995). Therefore, minimizing NH_3 losses is essential for a proper and effective use of slurry.

Climatic conditions, especially temperature, windspeed and precipitation, strongly influence NH_3 volatilization (Horlacher and Marschner, 1990; Sommer *et al.*, 1991). Field experiments aiming at a reduction of N losses from slurry and other animal wastes therefore need a technique measuring NH_3 source strength under ambient climatic conditions.

In plot experiments the microplot method (Kissel *et al.*, 1977) or wind tunnel systems (Lockyer, 1984; Braschkat *et al.*, 1993) can be used to quantify NH_3 losses. Both methods use volatilization chambers placed on the ground. Ammonia volatilization is calculated from the increase of NH_3 concentration in an artificial air flow passed through the chamber. Microclimatic conditions are disturbed by the chamber, as it excludes ambient wind and precipitation from the measured surface. In wind tunnel systems, microclimatic conditions can partly be adjusted to outside conditions by adjustment of air flow inside the chamber to windspeed outside. Calm and rain, however, cannot be simulated (Mannheim *et al.*, 1995). Air flow adjustment requires costly technical equipment. Therefore the number of plots to be measured simultaneously may be limited, as it is restricted to the number of wind tunnels available.

To avoid the disadvantages caused by the enclosing chamber, we developed an indirect open measurement technique appropriate to plot experiments. The method allows in situ measurements of NH_3 volatilization on bare or cropped soils without restriction concerning plot number or weather conditions.

BASIC IDEAS AND CONSTRUCTION

The indirect method described here is based on the comparison between unknown NH_3 release rates of manured plots (R_m) and NH_3 sources of known strength (Fig.1). In addition to experimental plots, standard plots are established and release NH_3 at known rates (R_s) during the experiment. Standard

plots are provided with NH_3 gas cylinder, regulator and flow counter. Ammonia is passed into plastic tubing (commercial sewage tubing with plug connections; inside diameter 50 mm) near the soil surface. Air is pumped into the tubing as carrier gas. The gas mixture is realeased through small holes drilled into the tubing (diameter 0,5 mm), approaching a two-dimensional source by a network of pointsources (four sources per square metre). The arrangement of tubing outlined in Fig.1 compensates for a possible pressure drop with increasing tube length by placing strong sources (short tubing) next to weak ones (long tubing).

At each plot a NH_3 sensor is placed leeward near the ground (e.g. 0,25 m above ground). We used passive samplers collecting NH_3 in sulphuric acid (10 ml, 0,01 M). Samplers consisted of roofed polyethylene containers covered with gauze to keep insects away. Ammonia collected as NH_4^+ is measured colorimetrically by means of a continuous flow analyzer (Alpkem RFA 300). These simple sensors provide a relative response to NH_3 concentration in the air. This is sufficient as will be shown below. Background-NH_3 concentration is measured windward. In the case of calm or unsteady wind sensors are placed in the middle of the plots, background signals being measured at some distance from plots.

The sensor signal of a standard plot (S_s) as well as that of a manured plot (S_m) may be related to the respective release rates (R_s, R_m) as follows:

$$S_s = B_s + p_s R_s \qquad (1)$$

and

$$S_m = B_m + p_m R_m \qquad (2)$$

with B_m, B_s: background signals of standard and manured plots, respectively

p_m, p_s: proportionality factors for NH_3 release from standard and manured plots, respectively.

The proportionality factor (p) is a function of both microclimatic conditions and plot design including NH_3 sensors. However, p is considered to be independent of NH_3 release rates (R). This assumption was tested by comparing the sensor signals of two standard plots measuring 2 x 5 m and being similar as to design and exposition but releasing NH_3 at different rates.

A low standard was adjusted to release 15 µg NH_3-N $s^{-1}m^{-2}$ (standard plot *a*) and a high one to release 63 µg NH_3-N s^{-1} m^{-2} (standard plot *b*). The plots were provided with two passive samplers each, one placed at 0,13 m, one at 0,23 m above ground. Additionally two samplers were installed windward for background measurement. The sensors were allowed to collect NH_3 for about one hour. Then a new measurement was started by changing sampler solutions. If p is independent of NH_3 release rates background corrected signals of the high standard will be 4.2 times the corrected signals of the low standard. Our results support this assumption (Fig.2).

Thus, we state that

$$p_m = p_s \qquad (3)$$

and combine eq. (1) and (2) to estimate R_m from R_s and background corrected sensor signals:

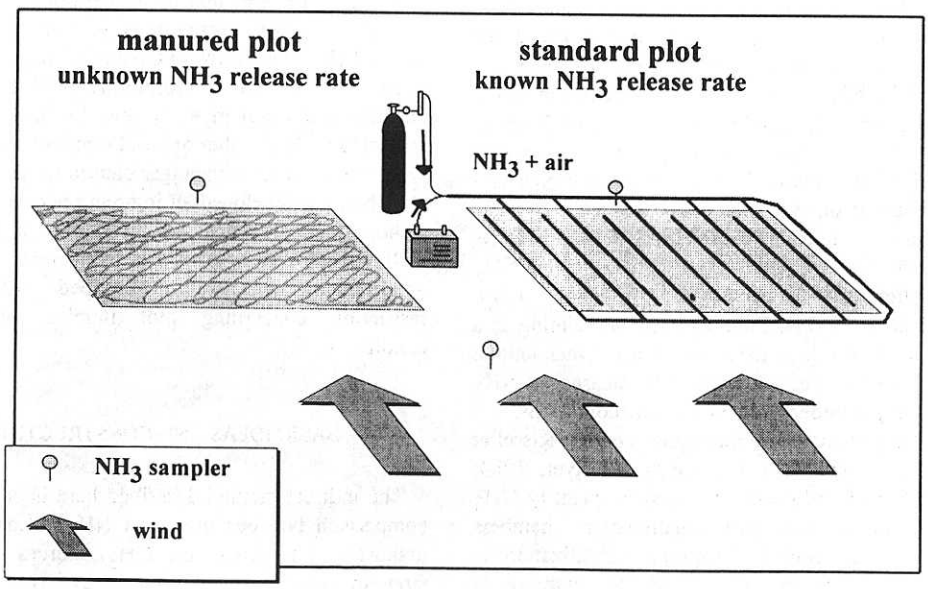

Fig.1: Schema of equipment for indirect measurement of ammonia emissions

$$R_m = R_s \frac{S_m - B_m}{S_s - B_s} \qquad (4)$$

Note that no absolute measurement of NH_3 concentration of air is needed for this estimation as it is based on the quotient of sensor signals.

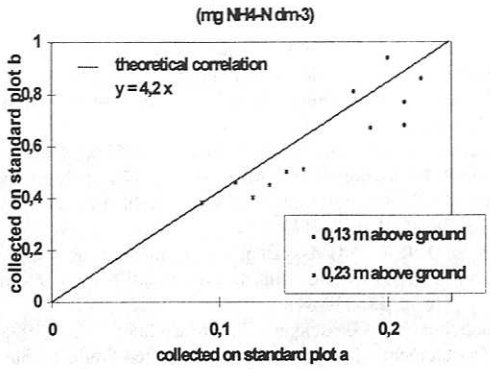

Fig.2 Sensor signals of standard plots a and b measured at different heights during measurement periods of 1 hour, NH_3 release rate of plot a being 4,2 times that of plot b.

FIELD STUDY ON NH_3 VOLATILIZATION FROM SLURRY

The method described here was used during practical operation in a field study of NH_3 volatilization from cattle slurry along with different application techniques. Measurements included comparisons between the passive NH_3 samplers described above and another sensor collecting NH_3 in washflasks.

Field plots equal to standard plots regarding size and exposition were established by applying slurry to areas of 2 x 5 m. Identical doses (2,4 dm^3 m^{-2}) of cattle slurry (1,14 mg NH_4-N g^{-1}) were broadcast, applied banded or carefully incorporated. Incorporation was done by passing slurry into cracks cut into the soil surface by metal hooks, a technique appropriate to cropped soils. Additionally, slurry was broadcast to plots sealed with plastic foil. The two standard plots (*a*, *b*) were adjusted to different NH_3 release rates (Fig.3). All plots were provided with passive samplers. Additionally, sensors collecting NH_3 by pumping air through sulphuric acid contained in washflasks were installed at manured plots and standard *b*. Equipped with a flow counter, this sensor allows absolute measurement of NH_3 concentration in air.

Fig.3 presents NH_3 amounts volatilized during 12 h as measured by comparison of sensor signals of manured plots with those of standard plots *a* and *b*, respectively. Comparison with standard plot *b* is presented for passive samplers and wash flasks. Measured volatilization hardly differed between sensor types, showing that relative response to NH_3 loading of air provided by passive samplers is sufficient for this measurement technique.

Application of slurry to sealed soil led to the highest NH_3 losses, followed by banded application. Incorporation was the best application technique regarding NH_3 conservation. The effects of application technique on NH_3 losses can be explained by the differing contacts between slurry and soil, increasing in the following order: broadcasting to sealed soil < banded application < broadcasting < incorporation. Low contact between slurry and soil resulted in high NH_3 volatilization, a finding that is in general accordance with literature (Amberger, 1990; Isermann, 1992).

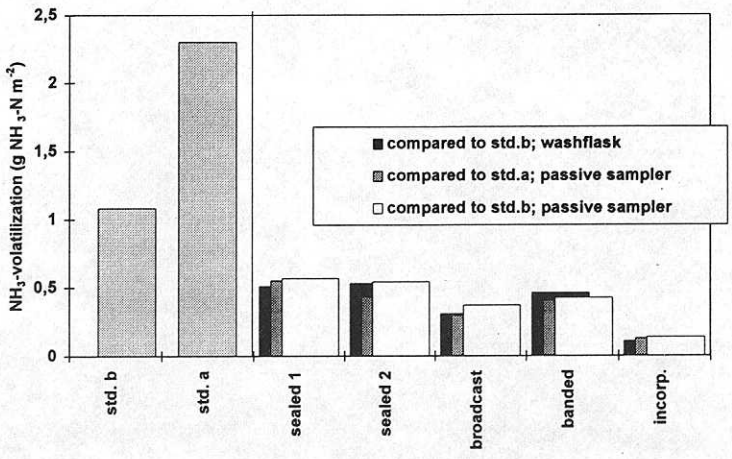

Fig.3: Ammonia volatilization from differently applied slurry, measured by comparison with NH_3 release of standard plots a and b, respectively, and with different NH_3 sensors (std. b = standard plot b; std. a = standard plot a; incorp. = incorporated).

CONCLUSIONS

The indirect method discribed here allows an open measurement of NH_3 volatilization from field plots without disturbing microclimatic conditions. As compared to wind tunnel systems, it is technically simple and cheap. An unlimited number of manured plots may be compared to one or several standard plots as long as the experimental design fits the basic requirements. Besides identical size and orientation of plots and sensors, homogeneous wind conditions throughout the experimentation site are required to allow indirect measurement. Since the measurement is open, it is recommended to keep some distance between plots and to ensure the absence of strong NH_3 sources near the experimentation site in order to avoid high background signals.

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CALIBRATION PROCEDURE AND AMMONIA MEASUREMENTS IN LIVESTOCK ENTERPRISES

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Abstract - Livestock buildings are one of the main sources of ammonia emissions. To evaluate the urgency and possible strategies for emissions reduction, measurements of ammonia concentration and the building air flow rates are necessary. The complex composition of the air in animal houses depends on parameters like house keeping, the live weight and the species of the animal itself and probably influences the result of a measuring procedure. To ensure proper measurements, a calibration with artificial air is required which is similar to that in real stables. Therefore a computer driven calibration device was developed and constructed, which enables the precise multi-level calibration of gas analysers or monitors by single- or multi-gas procedures. Recently an optoacoustic instrument and a FTIR spectrometer were calibrated. Sorption tubes and wet-chemical analyses were checked in certain steps of time.

In detail, NH_3, CH_4, N_2O, CO_2, steam and air (resp. N_2) are mixed in different concentrations for calibration purposes. The so calibrated instruments were used afterwards to measure in a piggery and a Louisiana-type broiler barn over several fattening periods. To study highly resolved temporal variations of the air concentration the optoacoustic instrument and the FTIR spectrometer were preferred because of their quasi-continuous ability. Air flow rates from the force ventilated piggery were measured directly by a fan-wheel-anemometer. Ammonia emissions up to 180 g hour^{-1} for the piggery concerned were detected for 517 pigs. The averaged live weight of the pigs was about 48 kg.

Keywords: ammonia, animal house, calibration, measurement, emissions.

1. INTRODUCTION

Ammonia and its effects may be considered in different ways. Indoor ammonia is a problem of animal and human welfare. Outdoor ammonia leads to local and mesoscale problems, such as nuisance by stench, building damages (Gronauer, 1993), soil N-input and plant harm. Agriculture, especially livestock is regarded as the main ammonia source. Estimations of ammonia emissions from German agriculture reach up to more than 80% of the total German emissions (Deutscher Bundestag, 1992). But in those estimations different calculation models and sometimes insufficiently validated databases lead to uncertainties and large variations. One reason for this is the lack of standardized measurement procedures. Moreover, difficulties arise from the measurement task and basically from the various parameters relative to the sources themselves. In general it has to be distinguished between point and non-point sources. Point sources are e.g. defined openings of forced ventilated livestock buildings. Non-point sources are storages or fields. Thus the detection of emission flow is needed. It can be measured directly by fluxmeters (passive samplers) (Carlson and Svensson, 1994) or by simultaneously applying air exchange and gas concentration measurement devices. Thereby problems arise in naturally ventilated buildings, for which only uncertain indirect methods like CO_2 or heat balance are available (van Ouwerkerk and Pederson, 1994). In conclusion, it is a fact that much research must be and will be done to get reliable values of ammonia emissions which enable the legislative to act in a satisfactory way. One commonly agreed base is the necessity of proper calibration of all instrumentation used. This paper introduces an example of a calibration device and the results of measurements in a piggery and a broiler barn.

2. CALIBRATION PROCEDURE

The complex composition of the air in livestock buildings depends on parameters of housing, feeding and the species of animals. Interferences between different gases sometimes lead to significant measurement errors, caused by the instrument or by the sampling materials, as shown by Krahl *et al.* (1996). To ensure a proper calibration this fact must be taken into account. As a first step to exclude measurement errors and to guarantee a multi-level calibration of different gases simultaneously, a computer driven gas mixing unit was constructed at the Institute of Biosystems Engineering (Figure 1).

Based on bottled gases with certified concentrations in the mixing chamber of the unit, certain concentrations of a single gas or a defined mixture of several gases are producable using computer driven mass flow controllers. Instead of purified dry air, N_2 was used as the carrier of the other gases. In practice, the humidity can influence the measurement procedure. Therefore, a controllable humidifier was added to the gas mixing unit which simulates the real humidity in livestock. A large range of concentrations in the final mixing chamber is guaranteed by controllable mass flows and certified basic concentrations. The current experiment concentrations for calibration are shown in Table 1.

It has to be pointed out that the calibration range should fit to the expected measurement values. Moreover, a calibration curve has to be given, that consists of a minimum 3 points - 2 at the ends of the range and one in the middle, especially if linearity is not expected.

Based on the artificial air from the gas mixing unit, not only different types of ammonia measurement instruments, but also the whole measurement procedure (sampling, filtration, transport and measurement) was evaluated. An optoacoustic device (Brüel & Kjaer 1302 Multi-Gas-

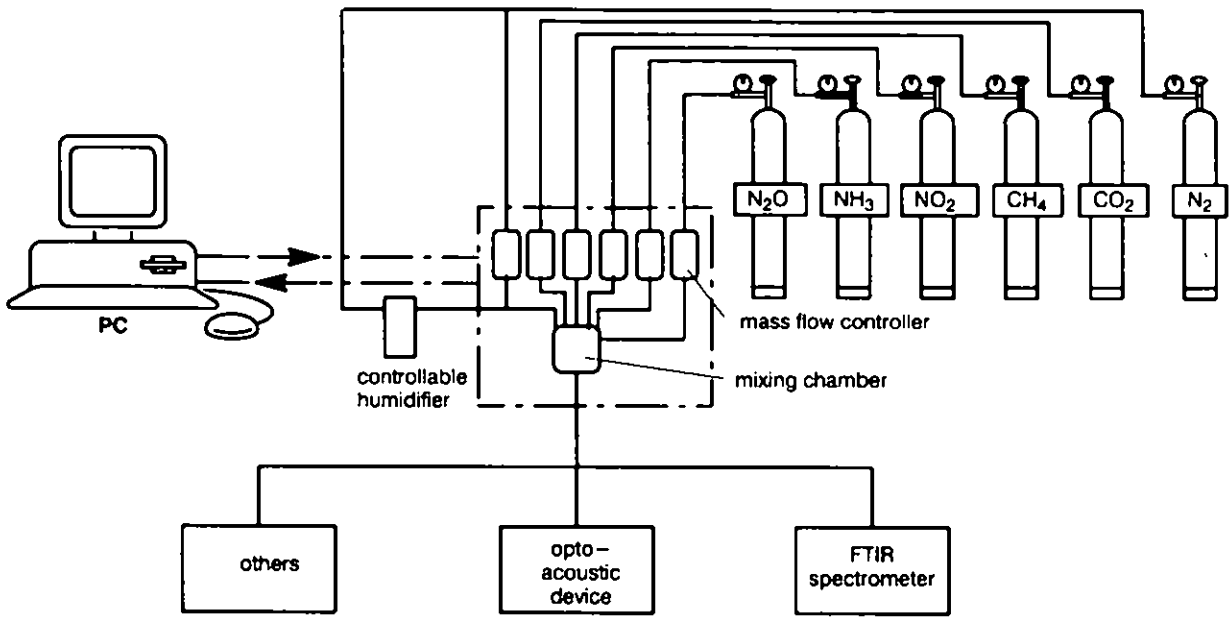

Figure 1: Gas mixing unit for calibration purposes.

Table 1: Current experiment concentrations for calibration

Gas	Concentration (ppm)	Flowmeter (ml min^{-1})	Total flowrate 2000 ml min^{-1}	Total flowrate 1000 ml min^{-1}	Total flowrate 700 ml min^{-1}
NH_3	184	200	max: 18.4 ppm min: 0.9 ppm	max: 36.8 ppm min: 1.8 ppm	max: 52.6 ppm min: 2.6 ppm
CH_4	1037	200	max: 103.7 ppm min: 5.2 ppm	max: 207.4 ppm min: 10.4 ppm	max: 296.3 ppm min: 14.8 ppm
N_2O	15.4	200	max: 1.5 ppm min: 0.1 ppm	max: 3.1 ppm min: 0.2 ppm	max: 4.4 ppm min: 0.2 ppm
CO_2	10100	500	max: 2525 ppm min: 126.3 ppm	max: 5050 ppm min: 252.5 ppm	max: 7214 ppm min: 360.7 ppm

Monitor), wet-chemical analyses (Dr Bruno Lange Küvettentest LCK 303) and sorption tubes (Dräger-Röhrchen Ammoniak 2/a) were verified and used to determine ammonia concentrations in livestock. Recently, an FTIR (Nicolet Magna-IR™ Spectrometer 550) was calibrated with the gas mixing unit and used for the ammonia quantification in laboratory and research stables. Because the FTIR spectrometer has the best optical resolution and the lowest interferences compared to the other measuring devices, this technique will be used as a reference further on. Figure 2 shows the results of 12-hour simultaneous measurements of ammonia concentration in a research reference stable under normal climate conditions, using the FTIR spectrometer and the optoacoustic device after a calibration with the gas mixing unit. The deviations in the calculated 30 min average NH_3 values are small.

3. RESULTS FROM ANIMAL HOUSES

Ammonia measurements have been carried out for a couple of years in a piggery and a Louisiana-type broiler barn in Lower-Saxony. Both farms are part of a comprehensive study being part of an EU-project about aerial pollutants in and from livestock buildings.

The broiler barn is naturally ventilated. Thus the air exchange cannot be estimated sufficiently at the present stage of research. Air quality investigations were only occupied with the measurements of the contaminants concentration (Hinz *et al.*, 1994). Looking for time dependent variations the multi-gas-monitor was used. To get a more sound database for the ammonia concentration, additional sorption tubes and wet-chemical analyses are used. Some results are given in Figure 3 for three periods of fattening.

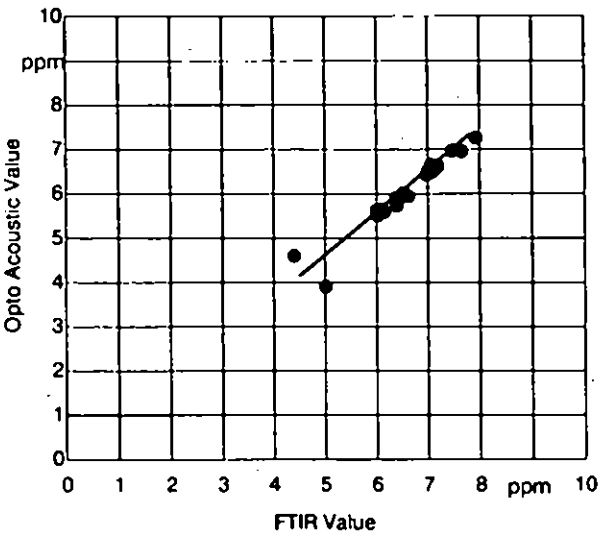

Figure 2: NH_3 correlation curve of 30 minutes average values from a measurement in a research reference stable.

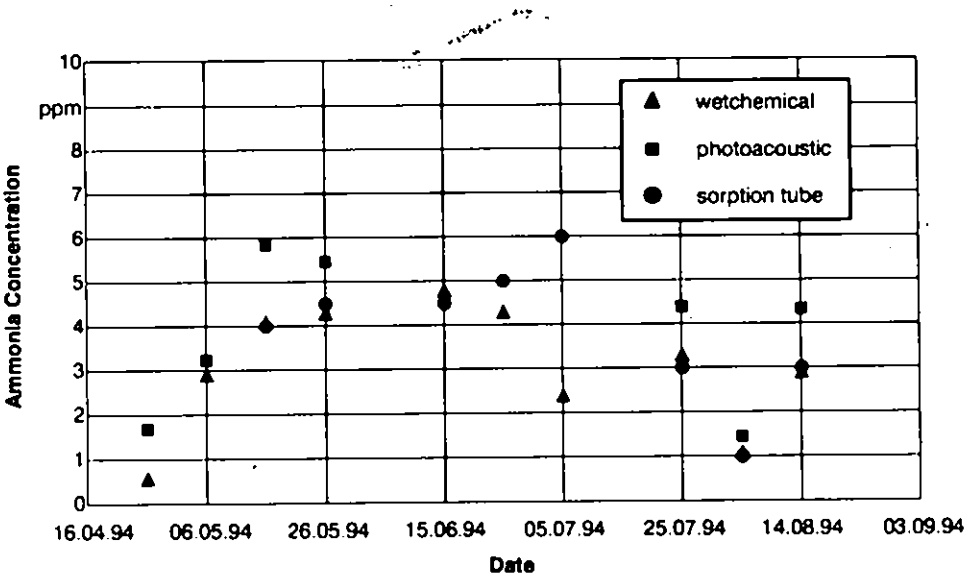

Figure 3: Ammonia concentration in a Louisiana-barn with a stock of 16000 birds.

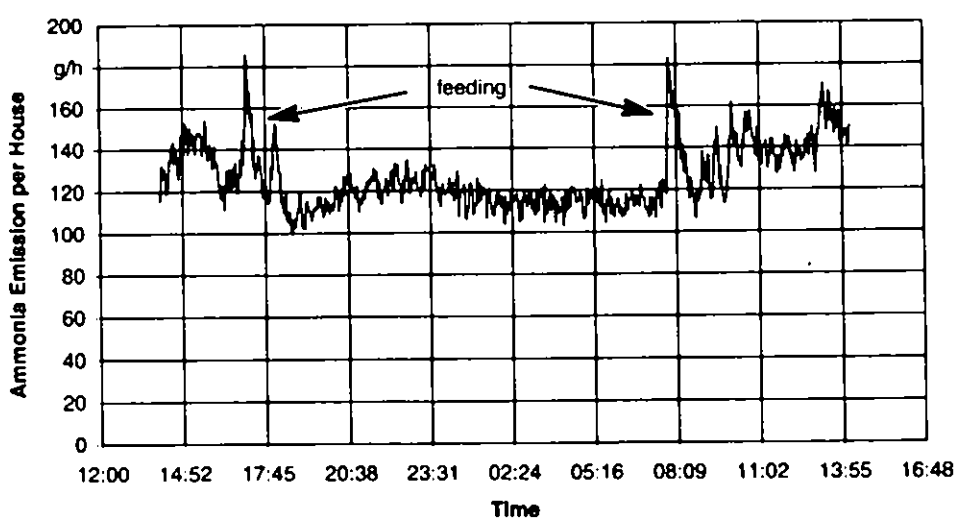

Figure 4: Ammonia emission from a pighouse with a stock of 517 pigs with an averaged live weight of 48 kg.

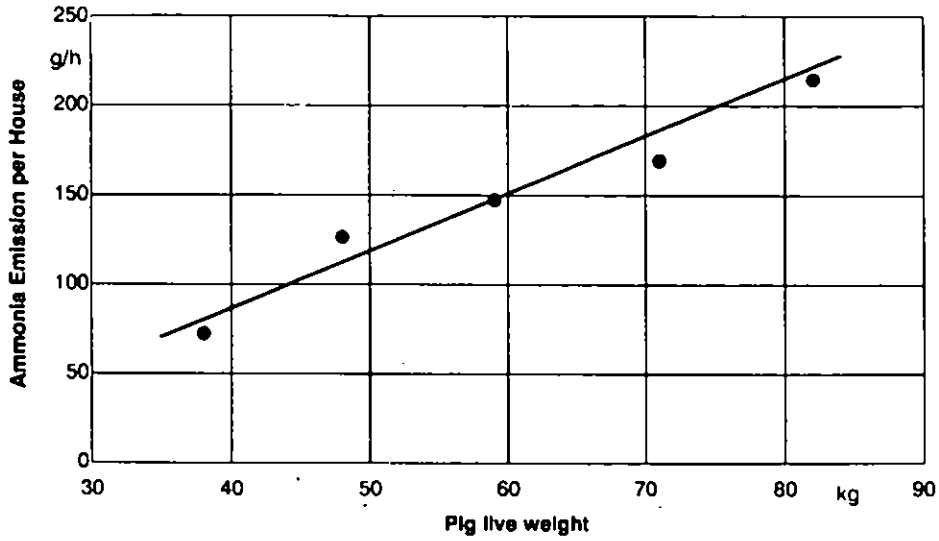

Figure 5: Ammonia emissions from a pighouse with a stock of 517 pigs.

Although the values of the different measurement techniques correlate generally quite well, the large deviations may be caused by unknown cross interferences. However, over the total run of 15 periods the concentration inside the broiler barn kept mostly to within the range up to a limit of 20 ppm. High values which occur in the beginning of a fattening period may result from litter handling and will be investigated extensively in the future.

The piggery investigated is forced ventilated by 5 axial fans in the roof of the building. The stock was 517 animals during the fattening period. The air flow was measured continuously by fan wheel anemometers in connection with a data logger (laptop). Ammonia concentration was detected by the optoacoustic device. The ammonia emission which results from both simultaneous functions of time is given in Figure 4 as an example with the 517 pigs, with an average live weight of 48 kg and for a period of time of one day. Typically the emission rate amounts 120 g hour^{-1}. The observable peaks of 180 g hour^{-1} per house result from feeding, which induces a high activity of the pigs.

Following the time of fattening it is relevant to notice that the ammonia emission increases with the pig mass. Figure 5 shows the 24 hour averages of ammonia emission versus the pig live weight from the above described piggery, determined by always the same optoacoustic instrumentation.

4. CONCLUSION

A computer driven gas mixing unit enables proper calibration of ammonia measuring devices with single gas and multicomponent procedures. Practical measurements require a frequent repetition of this procedure.

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AN OPERATIONAL MODEL FOR ESTIMATING AMMONIA FLUXES AFTER SLURRY SPREADING

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Abstract-Simulation models are convenient tools for estimating ammonia losses by volatilization after slurry spreading. They could assess the influence of environmental factors and agricultural techniques on emissions. A mechanistic model inspired from those of Rachhpal-Singh and Nye (1986) and Van der Molen *et al.* (1990) is proposed. It is based on a description of chemical equilibria between ammoniacal species and on water and nitrogen transfers in the soil under liquid and gaseous forms. Evaporation and ammonia fluxes are calculated on a hourly basis. This model requires only simple data as forcing variables : the soil pH, its initial soil moisture, meteorological data (solar radiation, wind speed, air temperature and humidity) and slurry characteristics (total amount, total ammoniacal nitrogen). Soil surface temperature is calculated from a soil surface energy balance. A sensitivity analysis was performed to enhance the most significant processes and the most influent parameters and variables. Calculated values were compared to measurements performed under actual field conditions. Both values are in fair agreement, together for the total losses and the time change on a hourly basis. The model has been then used to study the influence of environmental and agricultural conditions on the ammonia emissions.

Key word index: Ammonia, volatilization, modelling, slurry.

INTRODUCTION

Volatilization from slurry applied in the field is a major source of atmospheric ammonia. It depends on many factors related to soil, climate and slurry characteristics (Jarvis and Pain, 1990). Consequently, predicting ammonia emissions under any field conditions is difficult. Empirical modelling cannot account for the complexity of the pathway of all these factors (Sommer *et al.*, 1991). Mechanistic modelling is necessary to assess the influence of each variable on volatilization (Rachhpal-Singh and Nye, 1986; Van der Molen *et al.*, 1990). But the complexity of the required data makes its verification difficult.

The model that is proposed here, tries to make a compromise between the simplicity of input data and a realistic description of equilibria and transfers.

MODEL

Main features of the model

This model was inspired from those of Rachhpal-Singh and Nye (1986) and Van der Molen *et al.* (1990). It is a mechanistic model accounting for the heat, water and ammonia transfer in the top soil layers, and describing the equilibria between the different forms of ammoniacal nitrogen in the soil. The main features of this model are the followings :

- The relative proportions of ammonia and ammonium are calculated from the acido-basic equilibrium constant, and the equilibrium between gaseous and solute ammonia is obtained from Henry's law (Beutier and Renon, 1978; Hales and Drewes, 1979).
- Soil water transfers are calculated with the extended Darcy's law and soil hydraulic characteristics (porosity, hydraulic conductivity, water content at field capacity and at saturation, and matricial pressure) were deduced from a simple classification of soils according to their texture (Clapp and Hornberger, 1978).
- Ammoniacal nitrogen transfers through the soil layers are due to aqueous and gaseous convection and diffusion. The parameterization of the diffusion is the same as that of van der Molen *et al.* (1990).
- Evaporation and soil surface temperature were calculated by solving the energy balance of the soil surface using the parameterization of Noilhan and Planton (1989) for evaporation and of Cellier *et al.* (1996) for the soil heat flux. It only requires meteorological data and the hydraulic characteristics mentioned above.

- Volatilization is calculated with an advection model (Itier and Perrier, 1976). This allows to account for the local advection over little plots or at the beginning of slurry application.
- pH variations, adsorption by clays and organic matter of the soil and biophysical processes such as ammonification, nitrification and denitrification are neglected.

Calculation procedure

The model calculates the volatilization for several days to several weeks after slurry application with a data set comprising:

- soil texture, albedo, initial water content and pH; aerodynamic roughness length;
- slurry characteristics : total amount applied, ammoniacal nitrogen concentration, dry matter content;
- hourly meteorological data: solar radiation, wind speed, air temperature and humidity, precipitation..

Sensitivity analysis

The model sensitivity to different soil and model factors was investigated. For most factors, variations were large for the first day, but much less for the whole volatilization period. The total volatilization is limited by the availibility of ammoniacal nitrogen. The most sensitive factors are the soil pH (Fig.1.a), especially when it increased, and the depth of the first soil layer (Fig.1.b). There is no effect of the hydraulic conductivity. This allows us to use such a raw way to estimate its value.

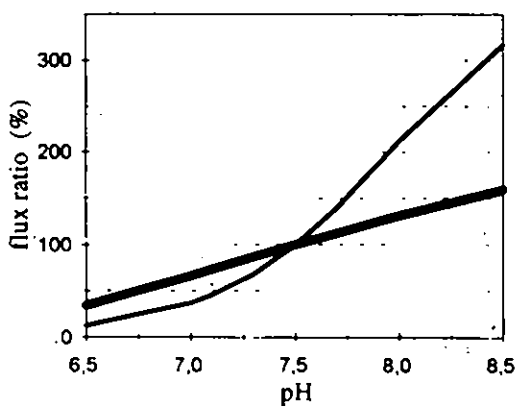

Fig.1.a Sensitivity analysis for the soil pH, for the first day (——) and for 10 days (▬). Y axis represents the ratio between the losses estimated for different values of pH and the losses estimated with the standard value (pH=7.5).

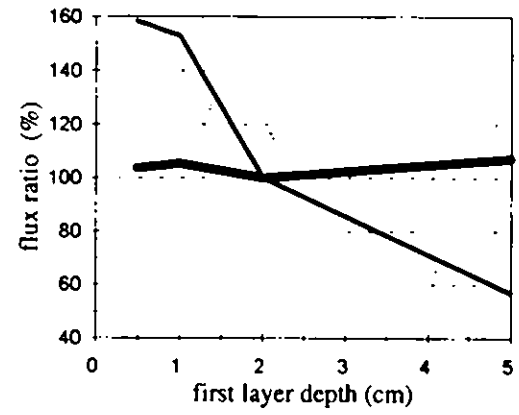

Fig.1.b Sensitivity analysis for the depth of the first soil layer, for the first day (——) and for 10 days (▬). Y axis represents the ratio between the losses estimated for different values of depth and the losses estimated with the standard value (0.02 m).

The influence of either the acido-basic equilibirum constant or the Henry's law constant is weak (resp. 2% for the first day and 0.5% over 10 days, and 20% for the first day and 8% for 10 days) compared with other factors.

RESULTS AND DISCUSSION

Comparison with measured emissions

The ammonia fluxes calculated with a pH of 7.8 were compared to the emissions of a surface-applied cattle slurry over an acidic soil in spring 1994, in Brittany (France). The emissions were monitored on a hourly basis with a mass balance method and a simplified aerodynamic method. The atmospheric ammonia concentrations were measured respectively with acid traps and with a chemiluminescence analyser. For more details, see Génermont *et al.*, (1996).

It can be seen on Fig.2 that the simulation is satisfactory for both the global amount and the daily and hourly behaviour of the ammonia emissions over a 11 days period. The fluxes are large during the day and low during the night, owing to the variations of surface temperature and atmospheric diffusion. This diurnal pattern is more pronounced with the model than with the measured values, especially for the first days. But except for these first days, the maximum values are well estimated. The gradual decrease from day to day owing to the decrease of ammoniacal nitrogen availibility is well described. The renewals of emissions for day 81 and day 85, which are due to changes in environmental conditions (Génermont *et al.*, 1996), are well described too.

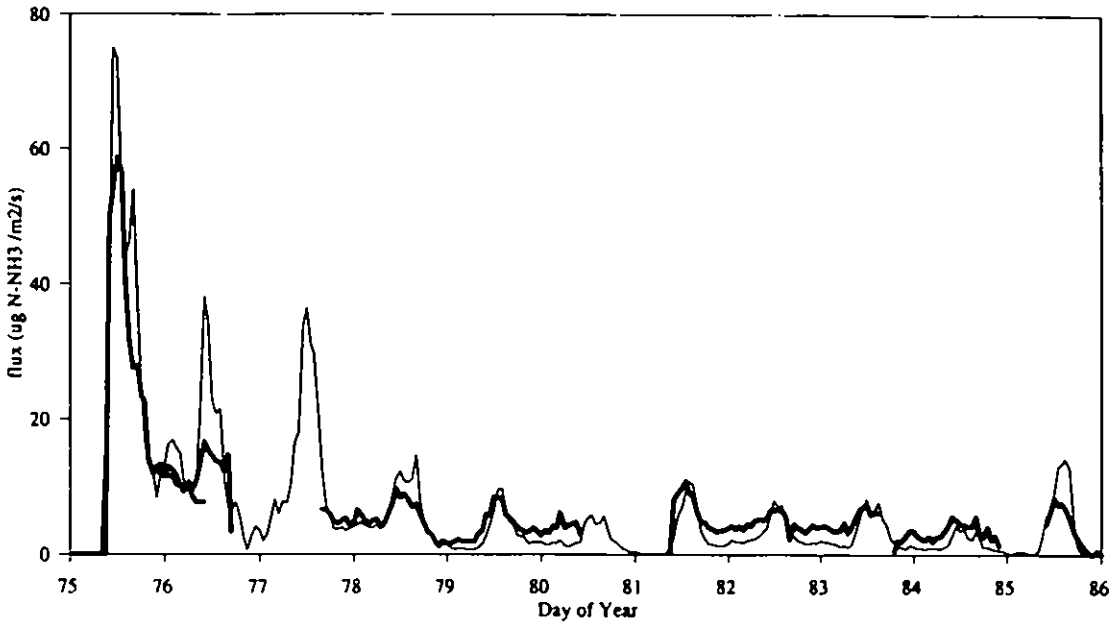

Fig.2 Measured (——) and simulated (——) hourly fluxes of ammonia over a 11 days period.

Using the model

Such a model can be helpful to predict the behaviour of ammonia emissions for changing local conditions of soil, climate or agricultural techniques. Calculations showed that likely variations in meteorological data could change the total losses by 10 to 20% (see for example solar radiation in Fig.3.a).

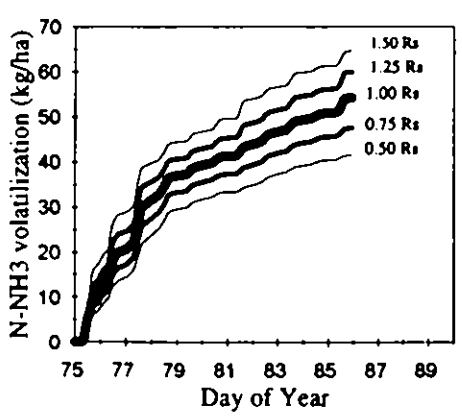

Fig.3.a Simulation of the influence of solar radiation on the cumulative losses of ammonia. Curves are obtained by multiplying measured solar radiation (Rs) with a coefficient between 0.5 and 1.5.

The effect of soil pH is much larger: the losses are doubled for an increase in pH from 7.5 to 8.0. Simulating a low fetch (e.g. measurement made with a wind tunnel) gave an increase of fluxes by 50% for the first day, but only 10% for the whole volatilization period (Fig.3.b).

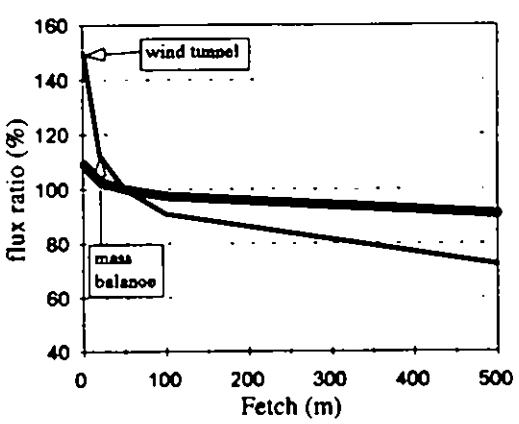

Fig.3.b Influence of the fetch on calculated ammonia losses. Y axis represents the ratio between the losses estimated for different values of fetch and the losses estimated with the standard value (50 m), for the first day (——) and for 10 days (——).

CONCLUSION

This model is adapted for operational use, but it would still require further validation over different soil conditions. It could also be improved by integrating some information on ammoniacal nitrogen adsorption on soil solid fractions and transformations due to microbiological activity as, for example, nitrification. It could also take into account the effect of the dry matter content of the slurry on its rate of infiltration into the soil. A strong improvement would be to predict the evolution of the pH of the soil-slurry complex, taking into account its buffering capacity and the rate of ammoniacal nitrogen dissociation (Avnimelech and Lahrer, 1977).

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Measuring ammonia emissions from stables with natural ventilation based on passive sampling.

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ABSTRACT

The application of a passive sampler is described to measure the ammonia emission of stables with natural ventilation. The measuring strategy, based on mobile sampling within the stable space, takes into account possible effects of over-estimating the ammonia concentration, due to agitation of animals during the sampling period. During the sampling period the sampler is compared to instruments measuring ammonia in an active way. The ventilation rate of the stable is measured by introducing in the stable a tracer gas at a known amount and, after mixing, determining the decrease of the tracer concentration in time (decay method).

Key word index: Ammonia, emission, natural ventilation, mobile sampling, sampling strategy.

Introduction.

Recently increasing attention was paid to the ambient ammonia concentration in air pollution studies. The variability of the ammonia concentrations on a regional scale is mainly a result of livestock farming: the different types of stables and the methods of field dressing with manure. The necessity of ammonia reduction has led to improvements of dressing methods and stable units; as a result the "green label stable" was introduced. The evaluation of the effectivity of the improvements made it necessary that the measuring methods should be representative for the environmental conditions. A Dutch working group "Measuring Methods Ammonia Emission from Stables"[1] carried out a study for the application of methods to stables with forced ventilation.
The recently developed passive sampling method of the Wageningen University (Willems badge)[2,3,4,5] has been accepted by the working group for indicative- and emission measurements and also for process monitoring and model validation.
More complex is the determination of emissions from stables with natural ventilation, where the ventilation of the stable is determined by the ventilation aperture of the walls and the ridge. The ventilation effectivity is determined by the outdoor wind velocity and -direction in relation to the geographic location of the stable and the conditions in the stable. The ammonia in the stable is dispersed by variable meteorologic and physical processes, what implies that within short distances in the stable considerable concentration differences may occur. Therefore it is of ultimate importance to sample enough sites in the stable to get a reliable figure for the estimation of the emission of ammonia. To fulfil this requirement an experimental setup has been introduced here by measuring ammonia in a mobile way: the samplers move slowly through the inner space of the stable, taking a spatially averaged sample. An extra advantage is that the measurements interfere as little as possible with the normal activities of the animals, since agitation may affect the emission level considerably.
The ventilation rate is measured by introducing a tracer gas into the stable and, after mixing, determining the decrease of the tracer concentration in time.

Measuring location.

The location is an up to date stable with natural ventilation and accommodates a population of about 400 goats. The overall cleaning cycle of the stable is 4 weeks, in which period the ammonia emission has to be measured during one day every week.
The stable's dimensions are 18.2 * 41 m^2. The volume of the stable is 4000 m^3.
The animals reside on floor grates, under which the manure is continuously split into solid- and liquid constituents which are drained off.
The ventilation aperture at both sides of the stable are 0.5 * 41 m^2 at a height of 2.5 m, and the air-outlet is situated in the ridge with a length of 41 m.

Measuring strategy.

Within a stable large spatial variation of ammonia concentrations occurs and mostly the sites of the ammonia sources can hardly be measured due to the presence of the animals. These conditions need a well-considered planning in relation with the objective of the study and adapted to the conditions of the stable space. Because passive samplers can operate independently and have a minimal weight, it is possible to implement the sampling in a mobile way. The samplers, hanging on a telpher-like construction traverse the stable at a speed of 1 $m.min^{-1}$ at a height such that the samplers cannot be reached by the animals. The construction of the telpher is chosen in such a way that the route of the samplers is representative with regard to the emitting spots. The measurement results in a representative spatial averaged concentration per sampler. In this way the true-to-nature circumstances in the stable are preserved and no extra ammonia by unwanted agitation of the animals is introduced.
For determining the ventilation rate the tracer gas SF6 is introduced in the airstream of a portable ventilator and quickly dispersed throughout the stable. The decay of the tracer concentration is measured at regular time intervals.

Measuring system and calculation.

The passive sampler consists of polystyrene parts guaranteeing no interactions with the ammonia gas.

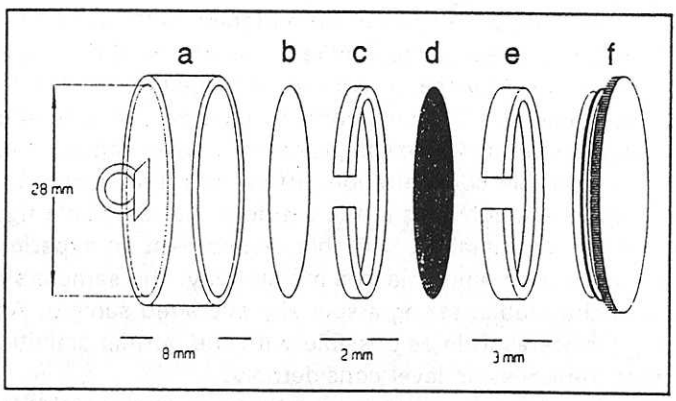

Fig.1 Design of the passive sampler (Willems badge).

Where:

a. Polystyrene sampler base.
b. Reaction filter.
c. Spacer.
d. Teflon membrane.
e. Fixation spring.
f. Polyethylene lid.

The basic part is a small circular vessel with a glass fibre filter on the bottom. The glass fibre filter is coated with tartaric acid that reacts with and immobilizes ammonia. A ring separates the reaction surface from a reinforced teflon membrane (Schleicher & Schüll, Te 38) causing a turbulent-free space.

The principle of the measurement is applying Fick's First Law to describe the process of diffusion and absorbtion. Taking into account the specific badge properties, the NH_3-concentration is calculated with

$$C_{av} = Q * R_t / (A * t) \qquad (1)$$

Where: C_{av} = averaged ammonia concentration ($\mu g.m^{-3}$)
Q = total amount of reacted ammonia (μg)
R_t = total badge resistance ($s.m^{-1}$)
A = cross sectional area of the badge opening (m^2)
t = exposure time (s)

Because in a stable the air movements are affected by the outdoor-weather conditions, the total resistance of the transport of the ammonia into the badge has to be determined empirically. As a reliable reference method the annular denuder was used. The actual badge resistance has the relation

$$R_t = C_{ref} * A * t / Q_1 \qquad (2)$$

Where: C_{ref} = ammonia concentration with the reference method ($\mu g.m^{-3}$)
Q_1 = reacted ammonia in the badge near the reference (μg)

For the determination of the ventilation rate the tracer gas is measured at six spots within the stable. During 18 minutes from introducing the tracer gas, the concentration is measured at 5 time intervals. The ventilation rate can be calculated from the tracer decay and can be described with

$$C_t = C_0 * e^{-kt} \qquad (3)$$

Where: C_t = tracer concentration at time t ($\mu g.m^{-3}$)
C_0 = tracer concentration at time zero ($\mu g.m^{-3}$)
k = decay rate (s^{-1})

The ventilation rate of the stable ($m^3.s^{-1}$) is the product of the decay rate (s^{-1}) and the stable volume (m^3).

EXPERIMENTAL.

Determination of the total badge resistance.

Simultaneously to the mobile sampling the calibration is carried out with denuders and badges in triple in the centre of the stable at a height of 1.8 m.

Week	Denuders		Badges				outside wind velocity ($m.s^{-1}$)
	C_{ref} ($\mu g.m^{-3}$)	r.s.d. (%)	Q (μg)	r.s.d (%)	t (s)	R_t ($s.m^{-1}$)	
1	770	2.3	11.40	2.5	4860	174	4.8
	671	1.1	8.88	5.2	4740	190	4.6
2	1244	3.4	14.75	5.9	4800	215	3.0
	1054	1.1	14.55	9.5	5100	196	4.3
3	2246	0.3	20.35	2.5	4740	278	2.4
	2763	1.0	27.59	4.3	4620	246	2.6
4	2730	3.3	21.99	2.3	3600	237	3.1

Table 1: Determination of the badge resistance, related to the measured outside wind velocity.

Averaged ammonia concentration of the stable.

The traverse of the telpher through the stable has been chosen in such a way that the conditions of the ammonia sampling are corresponding with that of the R_t-determination. Special attention therefore was paid to avoid draughty spots or gusts of wind near the ventilation aperture.

Week	Sampling interval (hr)	Q (μg)	r.s.d. (%)	R_t ($s.m^{-1}$)	t (s)	C_{av} ($\mu g.m^{-3}$)
1	10:15 - 11:36	18.37	4.0	174	4860	1239
	11:40 - 12:59	17.94	4.1	190	4740	1355
	10:15 - 12:53	35.70	1.8	182	9480	1291
2	10:30 - 11:50	22.86	5.9	215	4800	1928
	11:56 - 13:21	22.72	3.1	196	5100	1645
	10:30 - 13:19	45.69	0.7	206	10170	1743
3	10:42 - 12:01	28.16	2.6	278	4740	3111
	12:07 - 13:24	25.32	2.7	246	4620	2539
	10:42 - 13:25	50.03	0.8	262	9780	2525
4	11:15 - 12:15	25.44	3.4	237	3690	3078

Table 2 Averaged ammonia concentration.

During the stable measurements the outdoor ammonia concentration was between 21 and 48 $\mu g.m^{-3}$. The measurements were carried out by exposing badges at 2 m height during 4 hours at the weather-side of the stable. These ammonia concentrations are taken into account by calculating the emission of the stable.

Ventilation rate of the stable.

Week	Decay rate (k) at different sites (hr^{-1})						Avg V_r ($m^3.hr^{-1}$)
	A	B	C	D	E	F	
1	38.9	23.5	27.3	28.6	-	31.4	119600
	33.2	35.4	-	31.7	34.8	-	135200
2	41.7	38.7	37.1	34.2	39.0	37.1	152000
3	27.9	26.0	28.2	29.2	28.7	29.6	113200
	36.8	35.3	33.2	36.5	35.9	35.2	142000
4	43.5	36.2	33.1	32.5	34.3	34.9	137000

Table 3 Calculated ventilation rate (V_r) ($m^3.hr^{-1}$).

Estimation of the emission of ammonia from the stable.

The data of the tables 2 and 3 are used for the calculation of the emission of ammonia from the stable taking into account the outdoor ammonia concentration.

Week	C_w ($mg.m^{-3}$)	V_r ($m^3.hr^{-1}$)	Emission ($g.hr^{-1}$)
1	1.260	127400	161
2	1.737	152000	264
3	2.677	127600	342
4	3.057	137000	419

Table 4 Calculated ammonia emission.

Conclusions

The application of a mobile measurement technique with passive samplers offers a reliable estimation for the ammonia emissions of stables with natural ventilation. The measuring strategy is such that the behaviour of the animals is not disturbed so that unwanted ammonia emissions are avoided.
The determination of the ventilation rate by using a tracer gas has proven to be very adequate and practicable in this type of stables.
The measured emissions however are exclusively valid to the measuring periods.Emission data for longer periods can be attained with a more intensive measuring program.

The financial support of 'Hendrix Animal Food, Netherlands' is gratefully acknowledged.

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DEVELOPMENT OF A METHOD FOR CONTINUOUS AIR COLLECTION FOR MEASURING AMMONIA IN LIVESTOCK BUILDINGS

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Abstract - For quantification of ammonia emissions in pig fattening houses a reliable air collection system for continuous ammonia measurement has been designed. This system called "VECHTA" has been successfully used for collecting ammonia loaded air originating from pig fattening, poultry houses and bio scrubbers, respectively. Moreover, the system has been modified for air collection inside of naturally ventilated dairy cow houses. Based on that system, a continuous sampling of contaminated air is practicable for variable sampling periods of 15 minutes to 24 hour passage in the same bottle, with eight bottles on the whole system.

The system has been verified by calculating N-balances. Input: N-content in feed and piglets; Output: N-content in slaughtering pigs (115 kg LW), slurry and in the amount of ammonia emissions. In 34 pig fattening periods the input-output relations were in a range from 95 to 103%.

Key words: Ammonia emission, measurement technique, air collection system, livestock buildings.

INTRODUCTION

In some regions of Germany, emissions of ammonia originating from pig and cattle husbandry has become a serious problem. High rates of NH_3 volatilisation are partly a consequence of protein over-supply to animals. In addition, the techniques of slurry handling and storage indoors support high NH_3 emissions.

It was decided to carry out a detailed investigation programme studying the causes of ammonia volatilisation in pig and cattle husbandry more intensively.

OBJECTIVES

For the purpose of estimating the amount of ammonia volatilization in forced and naturally ventilated pig and cattle houses respectively, the first objective was to design a reliable air collection system for continuous ammonia measurement. According to the designed air collection for pig houses, the system has been modified for ammonia measurement inside of naturally ventilated cattle houses.

MATERIAL AND METHODS

For an exact ammonia quantification in different pig houses it seemed necessary to collect a sample of the ammonia loaded air during 24 hours each day over the whole fattening period. The air leaving the pighouse was sampled in the laminar area of the ventilation shaft in order to get a representative sample. The air collection system which has been developed is called "VECHTA". It is a totally redesigned system according to the so-called "MERRY GO ROUND SYSTEM", which has been developed in the Netherlands 30 years ago by TNO (Scholtens, 1992; personal communication). The system is controlled by a simple clock which switches remote valves at a certain preset time interval. The activated valves determine the air flow to the different bottles. A vacuum pump accounts for the air transport.

Air collection procedure in forced ventilated pig houses

The apparatus "VECHTA" is widely free from interference. It consists of two types of boxes. One is the so-called PUMP-BOX, of which there is only one per farm. To one pump box up to 6 bottle boxes can be connected, which collect the air samples.

The PUMP-BOX consists of a vacuum-pump, which is responsible for the actual flow of ammonia polluted air. The air flow is controlled by a gas meter. With the gas meter one can easily observe changes in the amount of air flowing through the system. An electric timer activates the valves which are located remote-controlled in the BOTTLE-BOXES. The bottle box contains 8 bottles, which are filled with sulphuric acid.

Each BOTTLE-BOX has a critical capillary, which controls the air flow to an amount of 1000 ml per minute. By means of the capillary the amount of air flowing through each BOTTLE-BOX is fixed. The capillary and also the vacuum pump is protected by a condensate drain with a dust filter in frost of each capillary. Furthermore there is installed a 10.000 ml per minute capillary as a by pass to relieve the vacuum pump.

The BOTTLE-BOX consists of an DELDRIN-block with eight valves. The timer in the PUMP-BOX allows an air passage into the same bottle between 15 minutes and 24 hours. Beneath each magnetic valve there is located a bottle filled with a sulphuric acid solution for each measuring period. This acid fixes the ammonia from the air. Because the whole is made out of a solid block of DELDRIN, there is a minimal chance for dead-space and leakage. Because there are eight bottles, it is easy to implement an on-week cycle, without disturbing any ongoing measurement.

To avoid water from the stable to condensate before the gas is being washed in the acid, the sample tube ('TEFLON') is extra isolated and electrically heated. Furthermore to protect the weak acid solution from freezing in the winter, the BOTTLE-BOX has been

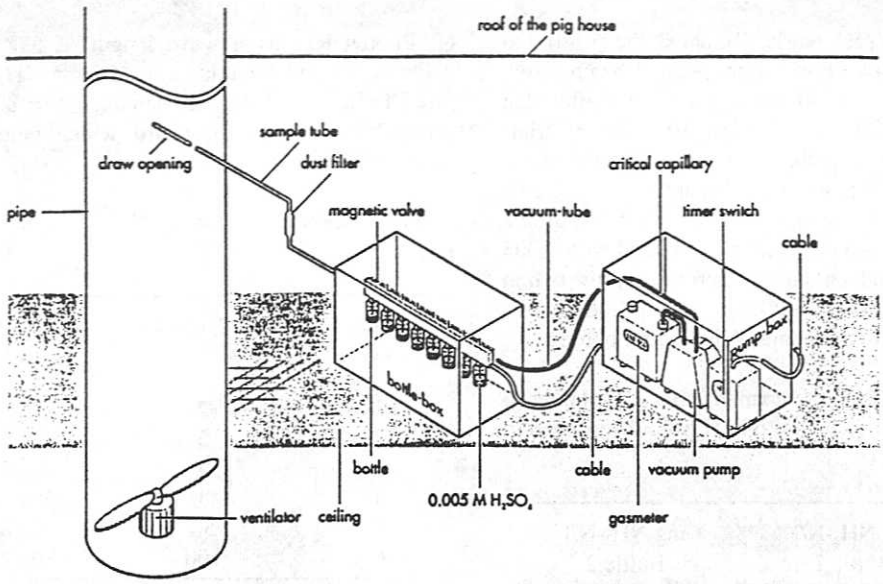

Figure 1: Air collection system "VECHTA"

additionally heated and isolated. The heating is controlled by a thermostat to 20°C. The tube from the BOTTLE-BOX to the PUMP-BOX contains also a condensate drain to protect the tube freezing in the winter.

The PUMP-BOX is located on a central point in the stable to serve the different BOTTLE-BOXES. The BOTTLE-BOXES are located as near as possible at the ventilation shafts (see Figure 1). By this way the distance from the sample point to the actual measuring process is only short.

Air collection procedure inside of naturally ventilated dairy cow houses

At half the height of the roof from each cattle house a special Teflon-tube-system according to van't Ooster (1992; Personal Communication) has been installed. Each 5 m it has been fitted with a critical capillary in order to collect an aliquot of wasted air - 500 ml min^{-1} per critical capillary. With in total 12 to 16 capillaries it has been ensured to get a representative sample of the polluted air (see Figure 2).

To protect each capillary against dust and dampness a PE-funnel with a diameter of 6.0 cm in front of each capillary as a dust filter has been installed. The funnel has been filled with cotton wool and closed with a gauze mech diameter 1.5 mm to keep flies and other kinds of insects away.

The system which transports the air continuously from each different spot - 12 to 16 critical capillaries - per house to the position where the ammonia will be bound is called 'LEER' and has been constructed according to the system "VECHTA". Contrary to that air collection system the DELDRIN block with the eight magnetic valves fixed on it has been installed directly behind the pump. In the dairy cow houses it was necessary to work with 300 ml of 0.005 M H_2SO_4 because evaporation rate is higher.

RESULTS AND DISCUSSION

Check up of the air collection systems

The actual fixing of ammonia is done by the sulphuric acid

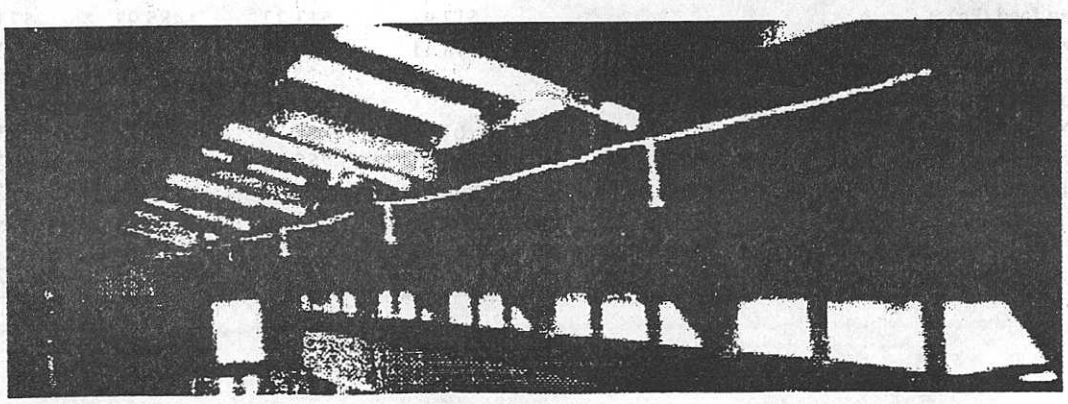

Figure 2: Teflon-tube system for air collection inside of cattle house.

(0.005 M) filled in each bottle. To check the absorption rate of the boxes, two boxes were located behind each other and the air was led through one and after that through a second bottle. During 10 different trials (percolation time per bottle 4 hours) less 0.58% of the total ammonia-N was found in the second bottle (Table 1).

Table 1 shows the ammonia-N content (mg/l) after a 4 hour air passage into the same bottles filled with 0.005 M sulphuric acid which has been determined in the two in series connected BOTTLE-BOXES. The results show a very high recovery of ammonia-N in the first bottle.

Table 1: Ammonia-N content (mg/l) after percolation of ammonia loaded air (4 hours) into H_2SO_4, determined in bottle 1 and 2.

Trial (N=3)	mg NH_4-N/l Bottle 1	mg NH_4-N/l Bottle 2
1	77.2 ± 1.3	0.2 ± 0.006
2	70.8 ± 1.5	0.3 ± 0.005
3	57.9 ± 1.0	0.3 ± 0.005
4	55.2 ± 1.0	0.3 ± 0.004
5	48.9 ± 0.8	0.2 ± 0.004
6	57.1 ± 1.2	0.3 ± 0.002
7	38.5 ± 1.2	0.2 ± 0.002
8	33.7 ± 0.9	0.1 ± 0.003
9	17.2 ± 0.7	0.1 ± 0.003
10	17.9 ± 0.7	0.1 ± 0.002

Analysis of ammonium sulphate

Ammonia is bound as ammonium sulphate. The ammonium sulphate is quantitatively analysed by forming an indophenol complex by a modified Berthelot-reaction (MERCK Spectroquant Test Combination 14752). Measuring was done with an autoanalyzing photometer (EPPENDORF) by a wave length of 578 mm. The calibration curve includes 2 to 100 mg NH_4-N per litre (see Table 2). Table 2 demonstrates a very high repeatability of each standard which belongs to the calibration curve.

Table 2: Calibration curve of NH_4-N including 2 to 100 mg/l.

Standard (n=3)	mg NH_4-N/l	ME1
1	2	27.5 ± 0.12
2	5	68.6 ± 0.71
3	10	132.5 ± 1.01
4	20	253.3 ± 1.35
5	50	567.8 ± 2.56
6	100	862.7 ± 4.43

1 ME milli-extinctions

N-balances

The system has been verified by calculating N-balances: The nitrogen input was calculated by the N-content of the piglets and N-content of the applied feed, the nitrogen-output by N-content in the slurry, N-content in slaughtering pigs (115 kg LW), N-content in lost animals, which died during the fattening period and finally N-content in the amount of ammonia emissions. Table 3 shows the results of these N balances.

Results of Table 3 elucidate the N-flow of a fattening period for four compartments as well as for the input compounds piglets and feed as for the output slaughtering pigs animal losses and the amount of emitted ammonis for these fattening periods. The results of these N balances are between 95.94 and 101.73% for the examples shown. These demonstrate that the N-flow has been quantified accurately.

Table 3: N-balances calculated for 88 fattening pigs per compartment, equipped with slatted floor, fresh air supply with partly-open glide flaps and polluted air removement above floor.

Compartment	1	2	3	4
N-input piglets (kg)	80.20	74.70	68.99	119.04
N-input feed (kg)	517.91	513.72	485.92	573.38
N-input total (kg)	598.11	588.42	554.91	692.42
N-output:				
NH_3-N emission (kg)	61.58	77.78	81.71	63.77
Slurry N (kg)	255.63	255.86	215.62	322.19
Slaughtering pigs and lost animals N (kg)	256.59	264.93	255.74	292.22
N-output total (kg)	573.80	598.58	553.07	678.19
N-balance relation output (%) input	95.94	101.73	99.67	97.94

Table 4: Mean values of N-balances per pig per day. Technical equipment of each compartment: slatted floor, partly open glide flaps, air removement above floor.

Compartment	1	2	3	4
N-input total kg (115 kg animal)$^{-1}$ day^{-1}	5.94	5.71	5.59	5.78
NH_3-N emission kg (115 kg animal)$^{-1}$ day^{-1}	6.49	7.10	8.23	5.39
NH_3-N emission total kg (115 kg animal)$^{-1}$ day^{-1}	0.71	0.86	0.94	0.64
Slurry-N (%) of N-output	44.55	42.75	38.99	47.51
Growth rates (%) of N-output	44.72	44.26	46.24	43.09
NH_3-N emission (%) of N-output total	10.73	12.99	14.77	9.40
NH_3-N emission (%) N-input via feed	11.89	15.14	16.82	11.12
Air removal (m^3 animal^{-1} day^{-1})	481.60	726.46	797.51	541.57

To ensure a direct/real comparison between the 34 fattening periods it has been necessary to correct all data to an animal's live weight of 115 kg.

It was observed that the amount of ammonia emissions all in all, including other data (not shown) equate to 7-20% of the nitrogen input via feed.

CONCLUSIONS

The systems allow an exact continuous air collection in order to determine ammonia concentration in the waste air of livestock buildings.

The analysis of ammonia via autoanalyzer (EPPENDORF; MERCK) ensures a quantitative analysis with very high recovery and repeatability rates.

These are really important instruments for carrying out exact calculations in purpose quantifying ammonia emissions in pig fattening houses and for dairy cow houses.

INVESTIGATIONS ON CONCENTRATION AND EMISSION OF AMMONIA IN KEEPING FATTENING PIGS ON DIFFERENT DEEP LITTER SYSTEMS OR ON SLATTED FLOOR BY MULTI-GAS MONITORING

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Abstract - *In situ* composting of pig manure (also known as deep litter keeping with additives - dl) was introduced in Europe to provide a welfare-positive bedded system which improves pig performance and eliminates effluent disposal problems. To evaluate gaseous emissions, continuous measurements considering daily dynamics of ammonia, nitrous oxide or other components are necessary. The objectives of these investigations were to use a new gas detection technique (multi-gas-monitoring) in measuring NH_3 concentration in deep litter or slatted floor (sf) keeping of fattening pigs.

Keywords: ammonia, nitrous oxide, carbon dioxide, multi-gas-monitoring, pig, deep litter keeping, slatted floor keeping

MATERIALS AND METHODS

Two rooms of a controlled environment house at the Veterinary Faculty of the University of Leipzig were used. Each chamber was assigned at the start of the experiment to the treatments:

1st growth cycle: ENVIROZYME deep litter system (dl)
fully slatted floor system (sf)

2nd growth cycle: ENVIROZYME deep litter system (2nd time of using)
ECOZYME deep litter system.

Each pen was stocked with castrated male pigs at a rate recommended for dl systems (1 pig m^{-2}) with 20 pigs per group. Each pen was managed in accordance with the setting up and maintenance recommendations of the companies supplying additives (1.5 ml ENVIROZYME per m^2 and week; 40 g ECOZYME powder per m^2 and week). Room temperature, relative humidity and ventilation changes were recorded by data logging of these parameters in the climate computer tests 3280 (Ahlborn Co.). Ammonia (and additionally carbon dioxide and nitrous oxide) were continuously measured with multi-gas-monitoring on the basis of photoacoustic spectral analysis. Additionally three times a week NH_3 measurements with liquid chemical indophenol method (during 6 hours per day) (VDI direction 2461) and with ammonia tubes (Draeger Co.) Tool place. The multi-gas-monitoring system (Bruel & Kjaer Co.) Consists of multi-gas monitor 1302, multipoint sampler 1309, laptop and software 7300 (Hoy, 1995). Averages of weeks and means of the whole keeping period were calculated. On this basis and with known ventilation rates (48 up to 62 m^3 $hour^{-1}$ pig^{-1}) emissions of ammonia were determined. Pen design and keeping conditions were described by Hoy *et al.* (1994).

RESULTS AND CONCLUSIONS

The means of gaseous concentrations on average of keeping period (14 weeks = 98 measurement days = 2352 hours with appr. 7000 values) are shown in table 1. Concentration of ammonia in ENVIROZYME deep litter system was significantly lower (9.7, 9.5 ppm resp.) Compared to slatted floor system (13.2 ppm) and ECOZYME system (13.3 ppm) on average of keeping period. Nitrous acid concentration in dl systems was much higher (2 - 2.2 ppm) than in SF system (0.2 ppm, $P < 0.1$). Carbon dioxide concentration did not differ between keeping systems. Weekly means of NH_3 concentration increased from the 1st to the 10th week of keeping and then decreased, which may be related to rising ventilation rates up to the end of keeping period (Fig. 1). Results of NH_3 measurements with indophenol method and ammonia tubes were similar in level and tendency to the results of multi-gas monitoring.

Reasons for differences in NH_3 concentration between dl systems could be the following:

greater emission active surface in new ECOZYME dl system combined with differences in structure (used and chewed wood chips) and compaction of dl material

higher dry material content in ECOZYME dl, better chances for NH_3 desorption

worse function of the dry powder ECOZYME in comparison with liquid solution of ENVIROZYME.

On the basis of measured concentrations and ventilation rates gaseous emissions were calculated considering 98 keeping days per growth cycle and 3.5 growth cycles per year. The data are given in Table 2.

Table 1: Means of ammonia, carbon dioxide and nitrous oxide concentrations on average of growth cycles

	Growth cycle 1		Growth cycle 2	
	ENVIROZYME Deep litter	Slatted floor	ENVIROZYME Deep litter	ECOZYME Deep litter
NH_3 (ppm)	9.7[1)]	13.2[1)]	9,5[2)]	13.3[2)]
N_2O (ppm)	2.0[3)]	0.2[3)]	2.2	2.0
CO_2 (ppm)	1210	1168	1348	1358

[1), 2), 3)] $p < 0.01$

Table 2: Emission of ammonia and nitrous oxide in relation to keeping system for fattening pigs

	Growth cycle 1		Growth cycle 2	
	ENVIROZYME Deep litter	Slatted floor	ENVIROZYME Deep litter	ECOZYME Deep litter
Ventilation rate (m^3 $hour^{-1}$ pig^{-1})	48	51	56	62
Emission of NH_3 (g $hour^{-1}$ pig^{-1})	.33	.48	.37	.58
(Kg NH_3 pig $place^{-1}$ $year^{-1}$)	2.71	3.93	3.1	4.8
Emission of N_2O (Kg pig $place^{-1}$ $year^{-1}$)	1.43	.15	1.89	1.89

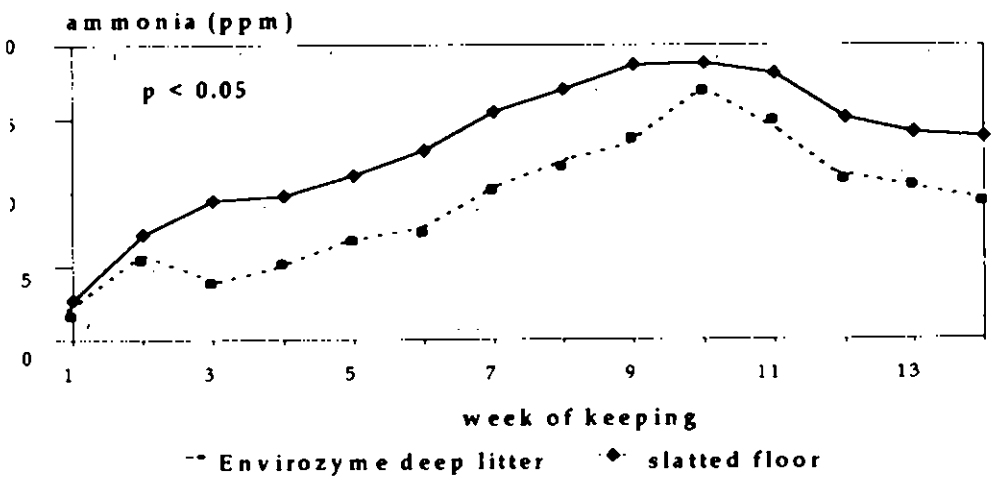

Fig. 1: Weekly means of ammonia concentration in deep litter and slatted floor keeping of pigs.

It is visible that emission of ammonia can be decreased by appr. 20 up to 30% by a good working deep litter system in comparison with full slatted floor keeping of fattening pigs.

CONCLUSION

Multi-gas monitoring is a method to measure continuously relevant from the view point of animal and environmental hygiene gases with high density and to calculate emissions. It has been shown that emission of NH_3 from an obviously good working deep litter system can be lower by 20 to 30% compared to traditionally slatted floor keeping system.

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HIGH PERFORMANCE SELECTIVE MEASUREMENT OF AMMONIA AND GREENHOUSE GASES BY FTIR SPECTROSCOPY

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Abstract - To determine the emissions of trace gases from animal houses, the FT infrared (FTIR) spectroscopy can be applied. This technique enables simultaneously for a precise quantification of at least CH_4, CO_2, NH_3, N_2O and H_2O. Therefore, via FTIR techniques the results of other commonly used measurement devices - e.g. those of optoacoustic types - can be evaluated.

Besides the analytical technique the sampling procedure is of importance, too. In particular, it must be considered that the sampling tubes should not be plastics or steel. In contrast, glass shows good results. To separate dust from the sample, filters of polypropylene should be used. Glass fibre filters failed, because NH_3 probably adsorbed heavily at their surface.

INTRODUCTION

The trace gas emissions from livestock are in the public focus, because they effect the environment and the quality of human life. In particular, ammonia (NH_3), laughing gas (N_2O) and methane (CH_4) are of special interest. Ammonia damages directly the vegetation and leads to nitrate and N_2O formation (Gisi *et al.*, 1990; Haber and Salazwedel, 1992). Methane and laughing gas contribute to the so-called greenhouse effect. Moreover, N_2O depletes the stratospherical ozone layer (Fabian, 1992). Emissions of steam (N_2O) and carbon dioxide (CO_2) are typical for livestock, too. However, they contribute to environmental effects only, when they originate from the consumption of fossil resources, e.g. energy for feed production and farm organisation. Besides the gases mentioned above, more than 130 other components were qualified in the exhaust of animal houses (Hartung, 1992).

Despite of this diversity, NH_3, N_2O and CH_4 are mainly relevant, because of their environmental effects and the total emitted masses. If it is the goal to reduce these components in agriculture, it is necessary to be equipped with a measurement technique which continuously enables for their quantification. Based on such results, different strategies in livestock are comparable and judgeable with regard to the environmental effects caused by the gaseous emissions.

The advantage of modern Fourier-transform infrared (FTIR) spectroscopy is to display the spectra of at least NH_3, N_2O, CH_4, H_2O and CO_2 simultaneously, because all these components absorb in the spectral infrared range (Griffiths and de Haseth, 1986). Moreover, other inferences with acetic acid or methyl amines are detectable and can therefore be excluded. The disadvantage of FTIR systems is their complexity. So they are not easily portable.

In practice, more handy facilities are desired. Lately, compactly constructed optoacoustic filter measurement devices are in use, which enable simultaneously for the quasi on-line detection of trace gases (Brunsch *et al.*, 1995; Klemet *et al.*, 1995).

In contrast to the FTIR technique, their spectral resolution is significantly lower. Moreover, it is commonly not possible to evaluate the measurement signals, because the results are exclusively displayed as concentrations, after some internal calculations.

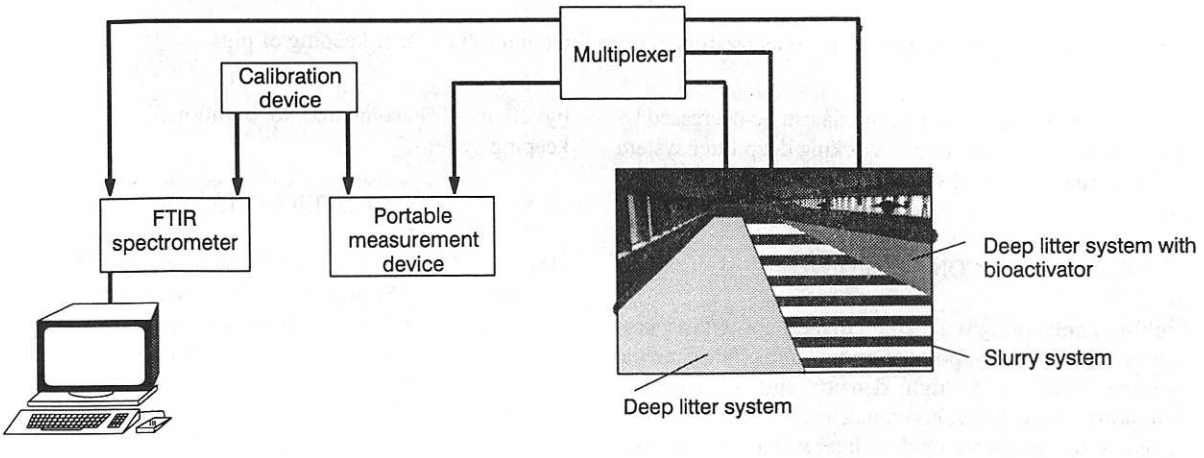

Fig. 1: Schematical view of the equipment at the German Federal Agricultural Research Centre.

The Institute of Biosystems Engineering of the German Federal Agricultural Research Centre has the opportunity to compare an optoacoustic system with an FTIR spectrometer in practice. To calibrate both, a computer driven calibration device is available. Using this facility it is also possible to judge the suitability of different materials for filters and tubes, which are necessary for sampling procedures in animal houses. Figure 1 shows a scheme of the equipment available.

OPTIMIZATION OF THE FTIR SPECTROMETER

At the beginning of the investigations, no comparable research by use of FTIR techniques in animal houses was known. Thus a gas cell with variable path length from 1 to 10 m was chosen. The FTIR device was a Nicolet Magna 550 with DTGS detector and an optical resolution of up to 0.125 cm^{-1}. Summing up the main results of the optimization procedure it can be stated that 8 m path length and 0.25 cm^{-1} optical resolution lead to good results. Thus an interference free detection of the trace gases mentioned above is guaranteed. Thereby, single separated, baseline resoluted absorption signals of each component can be taken for e.g. classical quantification procedures. In addition to the optimization and calibration of the FTIR spectrometer at the computer driven calibration device, the facility was compared with a gas chromatograph (GC). Table 1 shows the CH_4 and N_2O analysis of an air sample derived from manure by use of both techniques. The results are quite similar. NH_3 was not measured gas chromatographically.

Gas	FTIR Analysis (ppm)	GC Analysis (ppm)	Deviation (%)
CH_4	15.8	15.0	5.1
N_2O	2.2	23.3	4.5

Table 1: FTIR and GC results of an ani analysis derived from manure.

OPTIMIZATION OF THE SAMPLING TECHNIQUE

The sampling technique itself is as relevant as the analytical quantification technique. At first it was demonstrated that air from animal houses could not be sampled in bags which are carried afterwards to the analyser, because probably NH_3 was adsorbed at the inner surface of different bag materials. Even heated bags failed. Moreover, this adsorbing effect was reproduced at the calibration device. So a direct sampling procedure had to be chosen.

Nevertheless, tubes are needed, which lead an aliquot part of the air into the measurement devices. Because air from livestock is always dusty, filters are used to separate the particulate from the gaseous phase. Especially with regard to ammonia, the right choice of the materials for tubes and filters is of importance. Figures 2 and 3 demonstrate the effects of different tube and filter material towards ammonia. In detail, figure 2 shows the dynamic response of single, approx. 10 m long tubes according to stepwise changes of the NH_3 concentration. Glass and teflon (PTFE) tubes lead to the best results. The response of the pure gas cell - as figure 3 demonstrates - is quite similar to those of glass and teflon. But it has to be mentioned than an approx. 40 m long teflon tube lost approx. 1-2% of a 35 ppm NH_3 stream (V = 1000 ml/min). Moreover, a slight increase of water, caused by permeation from outside into this teflon tube was observed. However, the water content of the sample does not influence the NH_3 concentration measured by the FTIR spectrometer.

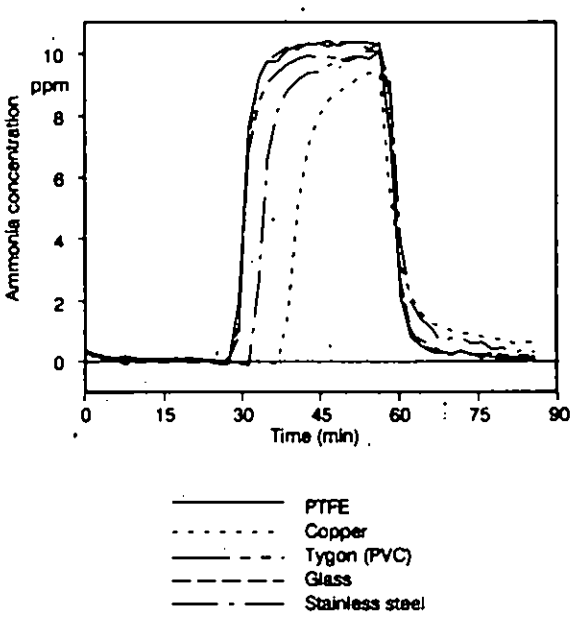

Fig. 2: Influence of different tube materials on the dynamic response of the measurements to stepwise changes of the NH_3 concentration.

Figure 3 points out clearly that the gas fibre filters or cellulose nitrate filters used led to non-sufficient results concerning NH_3 in comparison with other filter types.

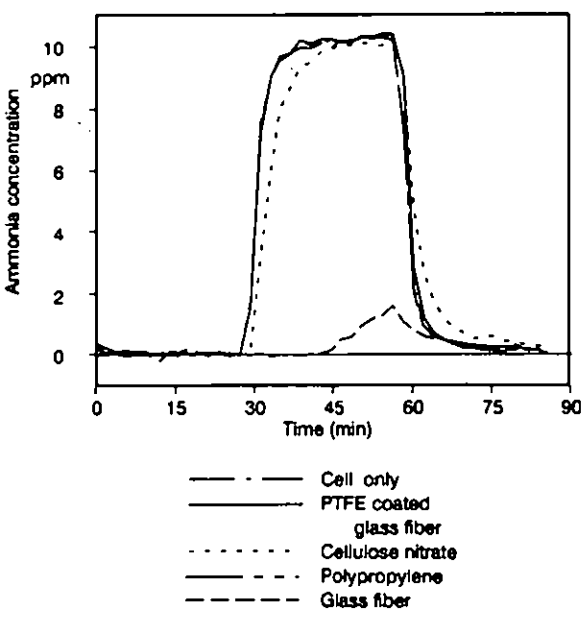

Fig. 3: Influence of different filter materials on the dynamic response of the measurements to stepwise changes of the NH_3 concentration.

COMPARISON OF THE FTIR SPECTROMETER WITH AN OPTOACOUSTIC MEASUREMENT DEVICE

In preliminary investigations at three piggeries (deep litter without and with bioactivator and slurry system) an optoacoustic measurement device, type Bruel and Kjaer 1302, was compared to the FTIR spectrometer. In detail, NH_3, N_2O and CO_2 showed sufficient conformity. Up to now the methane quantification did not always lead to satisfying results. Figure 4 shows a result of the measurement of ammonia with both systems at the different piggeries. The different NH_3 concentrations were approx. 1.6 and 9 ppm. It becomes obvious that the optoacoustic system did not always measure the exact values. Nevertheless, the total error was in the range of approx. 1 ppm.

CONCLUSIONS

The FTIR spectroscopy enables for the quasi continuous and simultaneous quantification of trace gases from livestock. However, also the right choice of materials for the sampling procedure is of importance. Glass tubes and polypropylene filters are most suitable. The FTIR technique allows to verify the results of other measurement devices. Therefore, it can be used for recalibration purposes, even if unknown, but interfering substances are contained in the gas sample. Normally, such effects cannot be eliminated by commonly used optoacoustic systems.

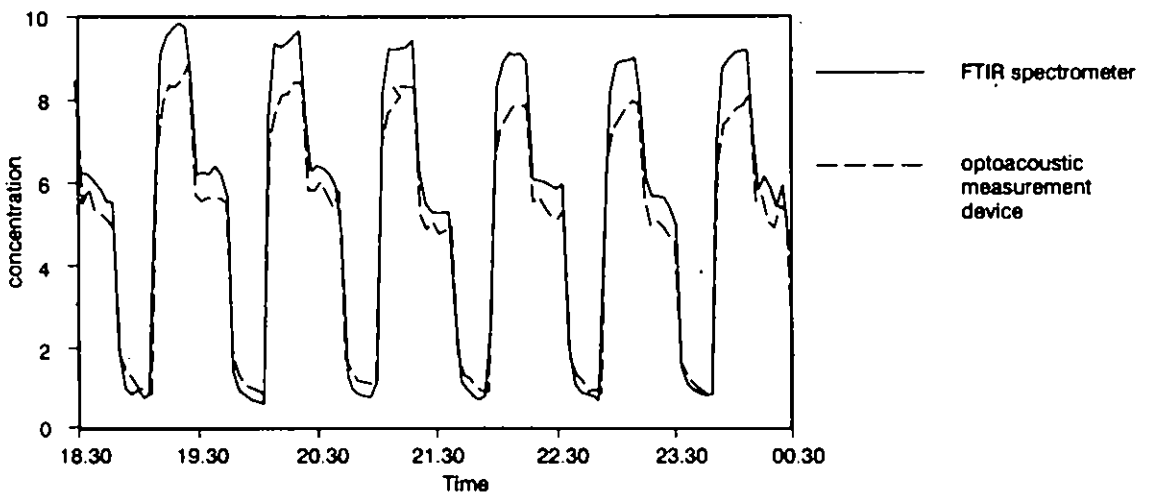

Fig. 4: Comparison of an ammonia measurement by FTIR and optoacoustic techniques.

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INVESTIGATIONS ON DYNAMICS OF AMMONIA CONCENTRATION IN RELATION TO MOTORIC ACTIVITY OF FATTENING PIGS AND BROILER CHICKENS

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EXTENDED ABSTRACT

Investigations took place in an air conditioned pigsty with two identical chambers (25 m^2 area and appr. 80 m^3 volume per room) and in a broiler house with three climatically controlled chambers (6 m^2 area and 15 m^3 volume). In one room of the pigsties a deep litter (d1) system on the basic of wood chips was installed. Once a week excrements of pigs were buried into d1 adding an additive ("BACTOSTIM"). Pigs of four rounds were kept on the same unchanged d1 system. In the second chamber a full slatted floor system with liquid manure storage during the whole keeping period was used. In every room 20 castrated male pigs were housed over a period of appr. 100 days from 25 to 105 kg under the same environmental conditions. Pigs were fed *ad libitum* by self-feeders with nipple waterers. Self-feeders were re-filled once a day at appr. 0700 hours. At the end of fattening period a second amount of feed were given in the afternoon.

Concentration of ammonia was continuously measured during three growth cycles (297 days) with a sensor technique consisting of a Quad Scan 6004 gas monitor and three gas transmitters 4485 with electrochemical sensors and electronical transmitter (EIT/USA). NH_3 values were continuously printed (LS 52/4 - LINSEIS, Germany). All hour-values were analysed by computer programme STATPAL and means of hours were calculated (Hoy *et al.*, 1992). Control measurements were done with ammonia tubes NH_3/2a (Dräger Co., Lübeck) three times a week and with liquid chemical indophenole method (German VDI - direction 2461) on three days per week from 0800 - 1300 hours.

Video recordings of the feed intake behaviour of baconers as indicator for locomotoric activity were made with an Infrared (IR) camera, IR lamp and time lapse recorder on four days at the beginning, at the middle and at the end of two growth cycles over 24 hours per day. The percentage of using self-feeders by pigs over 24 hours was computed. A high percentage of using troughs per hour is proportional to high motoric activity of pigs. Relationships between pig's behaviour on deep litter and NH_3 concentration were investigated by correlation/regression with programmes STATPAL and MEDIAST.

Investigations with broiler chickens took place on two deep litter (d1) systems with wood chips and additive ("ENVIROZYME") at the end of every round (one system with mixing d1 after slaughtering broilers - the other without mixing) and on straw. ENVIROZYME was given on the surface of d1 at the end of keeping period (1.5 ml per m^2). After these procedures a 5 to 8 cm layer of new wood chips was covered over used d1 material. Then the next growth cycle with one-day-chickens began. A total number of five growth cycles on the same deep litter system with increasing depth were carried out. In the third air conditioned chamber a straw system with cleaning after the end of every housing period was installed. The keeping conditions were described by Hoy and Kühnel (1995). Continuous measurements of ammonia were done in the 5th growth cycle with multi-gas-monitoring technique consisting of the multi-gas-monitor 1302, multipoint sampler 1309, laptop and software 7300 (Hoy, 1995). In the 3rd and 4th weeks of keeping, all hour values of NH_3 were calculated and means of hours over 24 hour-cycle on average of these two weeks were computed. Differences between means were analysed by multiple Newman/Keuls test.

RESULTS AND DISCUSSION

Results of continuous measurements of NH_3 with sensor technique in an air conditioned pigsties with deep litter for fattening pigs over three growth cycles with a total number of 297 days (appr. 7000 hour values) and of behavioural investigations during 576 hours in two keeping periods at the beginning, in the middle and at the end of thr growth cycle have shown a high congruence of both variables (concentration of ammonia; percentage of using self-feeders as indicator for animal motoric activity on d1 during a 24 hour cycle with characteristic biphasic dynamics and two periods of increased values (after morning feeding between 0700 and 0900 hours and in the afternoon between 1300 and 1500 hours) (Fig. 1).

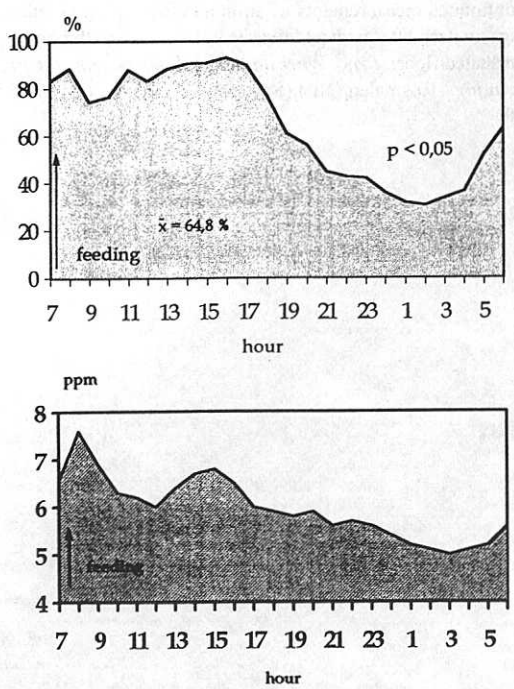

Fig. 1: Dynamics of motoric activity of pigs (top) and ammonia concentration (bottom) on average of 2 resp. 3 growth cycles during 24 hours in deep litter keeping.

An average of two growth cycles percentage of using self feeders by pigs was 68.4%. The hour averages of ammonia concentration and feed intake behaviour demonstrated a high significant positive correlation ($r = .83$; $p < .01$): concentration of NH_3 was increasing with increasing animal activity. The relationships between both parameters (NH_3 = y; percentage of stay at trough = x) were characterized by regression $y = 4.39 + .024\ x$. An increase of self feeder and by 20% increases of the ammonia concentration by 0.5 ppm. It seems, therefore, likely that motoric activity of fattening pigs especially rooting in deep litter leads to desorption of NH_3 from deep litter and to increased ammonia concentrations in the air of stable.

In broiler chicken housing on deep litter or on straw a significant relation between ammonia concentration and light-dark rhythm was also observed. An increase of NH_3 values by appr. 7 ppm during light period (0600 to 2200 hours) in comparison with dark period was found (Fig. 2). It is known that rest/activity behaviour of birds corresponds with the light regime. With increasing activity of chickens including pecking and scratching desorption of ammonia from the depth of deep litter material has been supported.

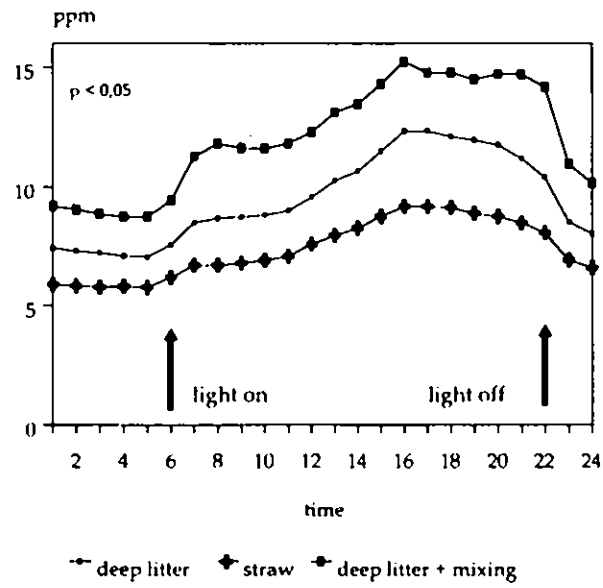

Fig. 2: Dynamics of ammonia concentration during 24 hours in keeping broiler chicken on deep litter with or without mixing or on straw.

CONCLUSION

To evaluate concentration or emission of ammonia from the view point of animal or environmental hygiene it is necessary to consider dynamics of NH_3 values in dependence on behaviour of animals. The variability of ammonia concentration during day and night period has to be observed in choosing representative measurement points or periods.

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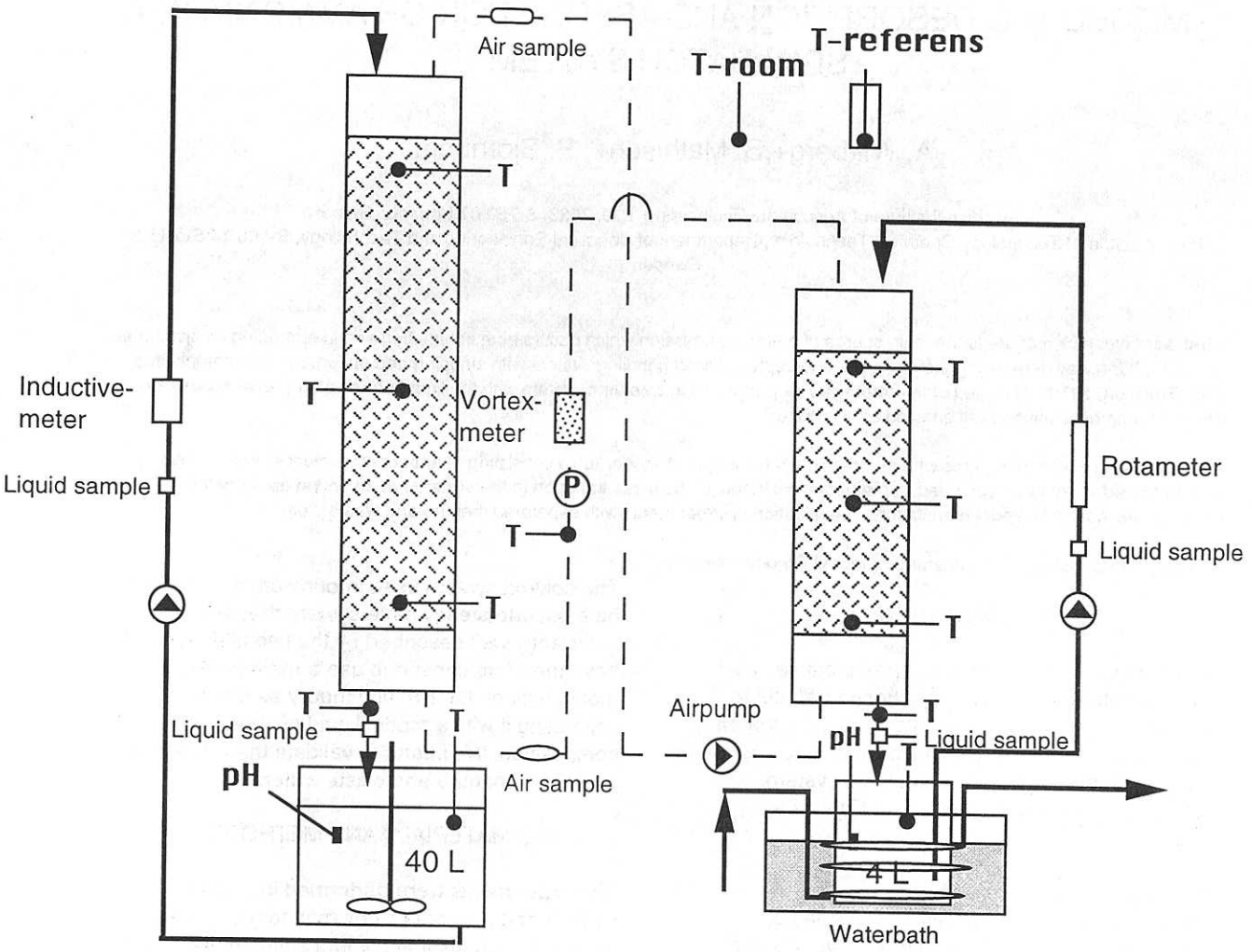

Figure 1.

RESULTS

The passage through the absorption column reduced the ammonia content in the incoming air by 99%. The remaining results obtained in the above conditions are presented in table 2.

Table 2 Comparing the reduction of ammonia at different initial pH.

Initial pH	Final pH ammonia	Reduction of
10.55	10.06	68%
9.70	9.18	50%

AMMONIA RECOVERY FROM LIQUID MANURE AND WASTE WATER - MODELLING DESORPTION AND ABSORPTION OF AMMONIA IN A SEMI-BATCH SYSTEM

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Abstract-Livestock manure is the main source of ammonia emission which occurs both in handling and in spreading (Buijsman et al., 1987). One way of reducing the emission is to apply a closed handling system with stripping and absorption of ammonia into acid (Trulsson, 1979). This kind of treatment can be performed in a column system with the liquid phase after phase separation. The acid-ammonia solution will be used as a fertilizer.

We have performed experiments with the mentioned technique. A model liquid consisting of ammonium chloride, sodium hydroxide and deionized water has been used. A mathematical model of the mass transport in the system has been set up. Together with the experimental data this model permits further evaluation of experiments with separated manure and waste water.

Key Word Index: Stripping, Mathematical model, Two-film theory.

INTRODUCTION

Ammonia emission to the atmosphere causes acid rain and eutrofied waters and is hence harmful to the environment. Large amounts of useful nitrogen is also spoilt. This problem could be reduced by stripping off the ammonia in a column system subsequently absorbing it into acid (Trulsson, 1979).

Stripping, or desorption, is a unit operation in chemical engineering that can be modelled by using the concept of the two-film theory. This is a steady state theory which is simple, but nevertheless it is often sufficient to properly describe complex phenomena. It was developed for physical desorption as well as for desorption with chemical reaction (Dankwerts, 1970).

In desorption/absorption with chemical reaction the desorption/absorption rate is usually related to the physical rate by an enhancement factor E (Dankwerts, 1970,Olander, 1960). Mass transfer coefficients, k_g for gas side and k_l for liquid side, are used as a measure of the resistance to mass transfer. The concentration gradients over the films are expressed as the concentration differences between bulk and interface on the liquid and gas side respectively.

The rate of mass transfer, J, can then be expressed as:

$$J = k_g(c^g_{bulk} - c^g_{\text{int}\,erface}) =$$

$$k_l(1+E)(c^l_{\text{int}\,erface} - c^l_{bulk})$$

The column system used in our work is assumed to be a pseudo-steady state system that can be sufficiently well described by the two film theory.We have therefore chosen to use a mathematical model built on the two film theory as a hypothesis, calibrating it with a model liquid of known composition. We intend to validate the model with separated manure and waste water.

MATERIALS AND METHODS

The experiments were performed in a closed system made up of two columns for desorbing ammonia and absorbing it into sulphuric acid. The columns were equipped with sensors for measuring temperature, pressure, liquid- and gas flows (see figure 1).

Desorption experiments were performed using a model liquid containing 0.2 M ammonium chloride, sodium hydroxide and deionized water. Sulphuric acid, 10% w/w, was used as absorption medium.

Process parameters for the experiments performed are summarized in table 1.

Table 1 Process parameters

Temperature	27 C
Liquid flow	0.200 $m^3 h^{-1}$
Gas flow	12 $m^3 h^{-1}$
Height of desorption column	1.65 m
Height of absorption column	1.19 m
Diameter of columns	0.10 m

So far we have tested two initial pH-values,10.5 and 9.7.

DISCUSSION

We apply the film theory to describe the momentary ammonia gradient over the column by integrating the mass flow J over the stripping column. Then we integrate over time and obtain information on the time needed for a certain reduction of ammonia. The corresponding modelling is done with the absorption column.

We are planning to use an ammonium chloride solution buffered by bicarbonate as a second model liquid.Using a bicarbonate buffered solution strengthens the similarity to other liquids because bicarbonate buffering is present both in separated manure and waste waters coming from the biological processes. In this way we can simulate the whole experimental system which enables the comparison of the behaviour of the calibrated mathematical model with that of the "real" liquids. Prediction of the amount of air and the amount of base needed for a certain reduction is then possible.

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ACKNOWLEDGEMENTS

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FUNCTION OF BIOFILTER IN CLEANING EXHAUST AIR FROM ANIMAL HUSBANDRY

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Abstract - A new type of downstream biofilter with seep water recirculation was installed for cleaning dust eliminated waste air from fattening pigs kept on a deep litter system.

Beside ammonia detection in crude gas and clean gas by indophenol method, test tubes (Draeger) and photoacoustic spectroscopy a continuous measurement of dinitrous oxid (N_2O) and carbon dioxide (CO_2) was carried out. Odorant concentration was determined by olfactometry. The determination of ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) demonstrates the deposition of possible metabolites of nitrification in the filter medium in different layers and in seep water.

Results show at a filter volume load of 115 $m^3/m^3 \cdot h$ an efficiency of 96,2 % - 100 % for NH_3 and 97,0 - 100 % for odour abatement. But only a small amount of calculated ammonia N-input of around 505 g could be found in form of NO_3^- (90 g), NH_4^+ (13 g) and NO_2^- (7 g) during a period of 165 days. The loss of nitrogen (N) couldn't be explained by releasing of N_2O.

Results are discussed in connection to microbial investigations concerning nitrification/denitrification activities.

Key word index: ammonia, nitrification, odour abatement, nitrogen balance

Introduction

With the recognition of ammonia as hazardous to the environment, its statutory limitation in emissions can be expected in Germany in the coming years.

Biological purification of waste gases by means of biofilters can be used in cases with air pollutants, which are biologically degradible. The decomposition of the pollutants is carried out by microorganisms selltled on a solid carrier substance (Bendinger 1992).

This technique is well suited for treatment of big off-gas streams with low pollutant concentrations. So the biofilter cleansing process is a widely used method of cleaning exhaust air from animal husbandry esp. concerning the reduction of odour emissions (Pearson *et al.* 1992).

Recently biofilters are discussed as a possible means for abating ammonia emissions from livestock farming, but there is no practical technology available (Mannebeck 1995, Rasmussen *et al.* 1994).

Descrption of biofilter trials

Figure 1 showes the principle of biofilter design during a period of trial of 165 days.

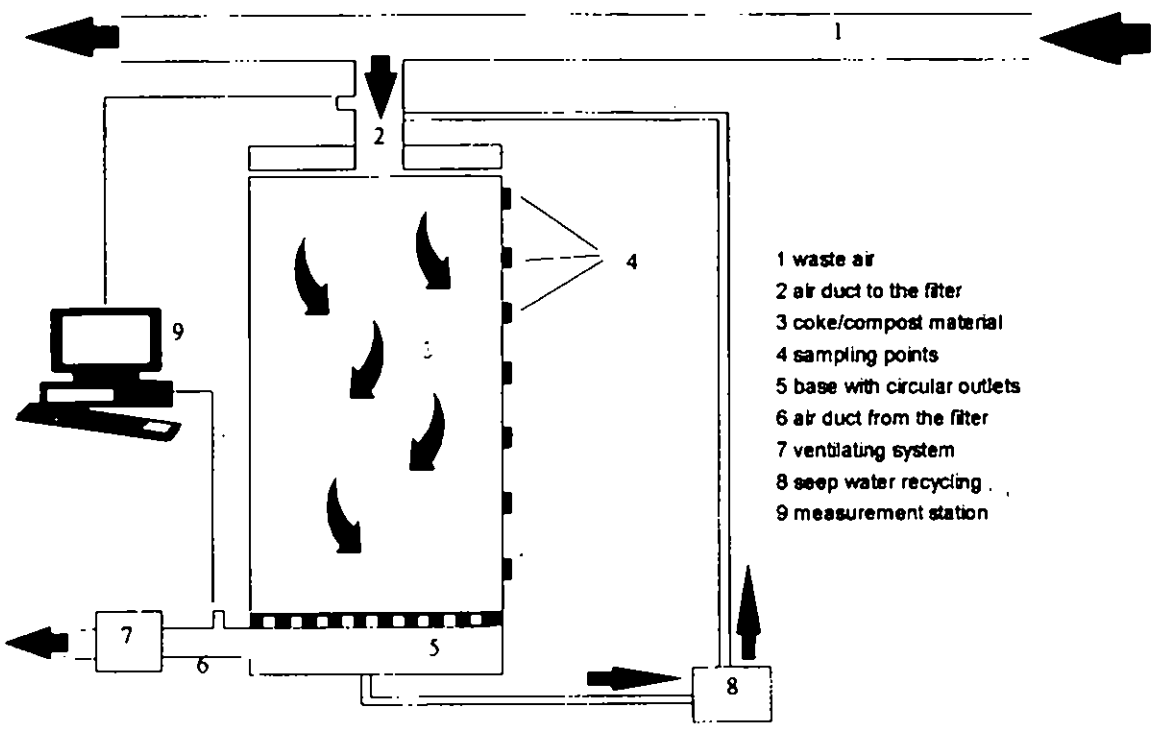

Fig. 1. Principle of biofilter design

Characteristics of the pilot filter:

The cylindric pilot filter chamber (made of plexiglas, 40 mm diameter) was filled in a bulk height of 140 mm (filter volume 175 l) with a mixture of activated coke (cylindric, 4 mm diameter) and mature compost (fraction < 3 mm) in a volume ratio of 1:1 The filter medium moisture content at the beginning of trial was 40 %, pH of fresh material was 7.1.

The biofilter was loaded with dust eliminated air from fattening pigs, kept on a deep litter system, at an air flow rate of 20 m^3/h, 115 m^3/m^3 * h resp. The air stream was characterised by temperature (14 - 28 °C) and relative humidity (32 - 85 %). Humidification of the packed bed was done by sprinkling water (daily inflow 0.5 - 4.0 l) on the top of the filter chamber and recirculation of seep water. The whole water requirement was 215 l for 165 days.

The residence time of gas in the filter varied between 6 - 8 s.

Measurement techniques

crude and clean gas:

NH_3: Draeger tubes for ammoina (type 2/a), indophenol method (VDI 2461/1, 1974), photoacoustic spectral analysis by 1302/1309 device (Brüel & Kjaer, DK)

N_2O, CO_2: continuously multigasmonitoring by 1302/1309 device

odorant concentration: according to VDI 3881/1-3 (1987), Olfactometer TO7 (Mannebeck, D)

temperature and relative humidity: continuously

gas flow: by calculation on the basis of air velocity

residence time in the filter: air current tubes

filter medium:

NO_3^-, NO_2^-,NH_4^+: in suspension of 5 g wet weight filter material in 100 ml 0.01 mol $CaCl_2$-solution after stirring 60 min and centrifugation following the sample procedure instructions of DR/700 colorimeter (HACH company, U.S.A.)

dry matter: weight of 5 g wet weight material after drying at 105 °C until constant weight

pH value: in suspension of 5 g wet weight material in 100 ml 0.01 mol $CaCl_2$-solution after stirring 30 min

Furthermore daily measurement of temperature in different filter layers and nitrate, nitrite, ammonium and pH-detection in seep water was done.

Results

The crude gas concentration of ammonia increased during a period of keeping fattening pigs and ranged between 2 - 33 ppm during whole trial. Figure 2 demonstrates the cumulative NH_3-N input into the biofilter on the basis of weekly determined avarage ammonia concentrations.

In clean gas the measurement with Draeger tubes gave a non detectable level of ammonia (<<1 ppm). By using indophenol method it was possible to find concentrations of ammonia in clean gas between 0.8 ppb and 1.02 ppm. The results from continuously measurement of ammonia with 1302/1309 multigasmonitoring weren't reliable because of absence of frequent recalibration which is nessesary esp. for good water soluble substances.

An efficiency of 96.2 - 100 % of the biofilter system concerning ammonia could be calculated on the basis of found concentration by indophenol method.

The weekly determined average concentration of N_2O was between 351 - 1665 ppb in crude gas and between 565 - 1619 ppb in clean gas. For whole duration of trial an avarage mean of

882 ppb in crude gas and 1049 ppb in clean gas could be calculated. That gives a total N-loss in form of N_2O of 18.5 g over the duration of 165 days.

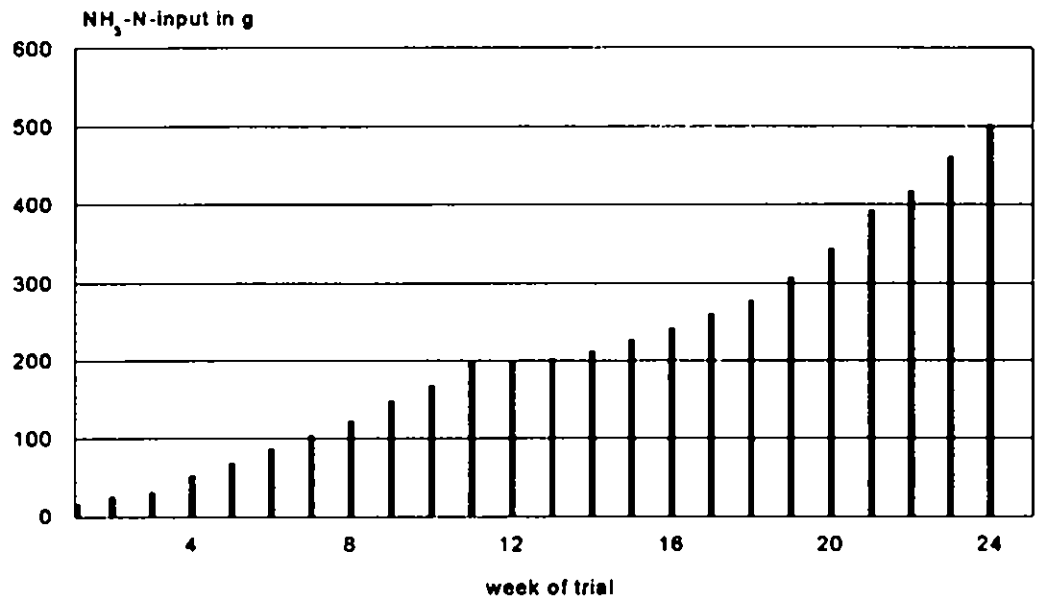

Fig. 2. NH_3-N input into the biofilter

The odorant concentration in crude gas varied between 19 - 480 o.u./m^3. The clean gas was odour free except one sample (7 o.u./m^3) so that the odour abatement was 100 %, 97.0 % resp.

The detection of NO_3^-, NO_2^-, NH_4^+ demonstrates the deposition of metabolites of nitrification process in the filter medium. From figure 3 one can see as an example the enrichment of NO_3^- in different layers. The development of deposition of NO_2^- followed the same tendency and showed after 162 days these levels of concentration: upper layer - 284.9 mg/kg dry matter; middle layer - 3.7 mg/kg dry matter; bottom layer - 3.8 mg/kg dry matter. Ammonium doesn't have such a steep enrichment, after 130 days no further increase in amount could be detected. At day 162 the following concentrations were determined for NH_4^+: upper layer - 484.0 mg/kg dry matter; middle layer - 71.4 mg/kg dry matter; bottom layer - 18.4 mg/kg dry matter.

A similar development of determined N-containing nitrification metabolites turned out in seep water with high enrichment of nitrate (up to 1830 mg/l) and nitrite (up to 14.9 mg/l), but no increase in ammonium concentration. Despite of these processes the filter material kept a pH-value between 6.5 (upper layer) and 7.1 (bottom layer). The pH in seep water decreased from 8.6 to 7.1.

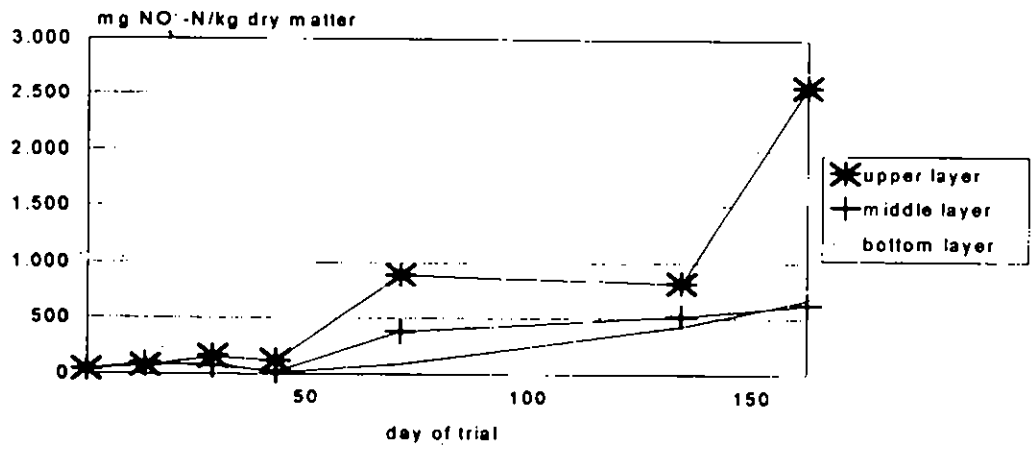

Fig.3. NO_3^- content of filter medium in different filter layers in dependence of trial duration

Conclusions

- Possibility of complete cleaning of dust eliminated waste air from animal husbandry concerning ammonia and odour on the basis of a new type of biofilter medium
- Suitability of downstream biofilter-operation with water recirculation (low water requirement) for this purpose
- High rate of nitrification up to 2500 mg NO_3^--N/kg dry matter of filter material
- Hypothesis of simultaneously occuring dentrification activities for explanation of around 75 % N-loss

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RESULTS OF AMMONIA MEASUREMENTS IN CHICKEN STABLES BY THE HELD OF MULTI-GAS-MONITORING

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Abstract - Housing broiler chickens on deep litter from wood chips with additives could give the possibility to reduce emissions of ammonia, odour and dust from broiler houses, to shorten service period (time for cleaning and disinfection) between growth cycles and to keep broiler chickens of a few keeping periods on the same litter material. The aim of our investigations was to determine concentrations of ammonia and nitrous oxide in different keeping systems for broilers.

MATERIAL AND METHODS

The investigations took place in three air conditioned chambers of a broiler house. The following keeping systems were investigated:

Chamber 1: deep litter (DL) system from wood chips; after the end of every round used DL was moisted with an additive (ENVIROZYME) and covered over with a 5-8 cm layer of new wood chips

Chamber 2: straw, with cleaning chamber after every growth cycle

Chamber 3: same procedure like in chamber 1, additional mixing DL material after the end of every growth cycle.

ENVIROZYME is a liquid solution of whey and water with soil bacterias, enriched with trace elements (Fe, Mn, Co, Zn, Cu). A dose of 1.5 ml m^{-2} litter was used.

100 one-day-chicken per chamber (18.2 m^{-2}) were kept up to slaughter with a mean age of 35 days. Microclimate was characterized by following parameters: temperature - 28°C decreasing (to 20°C), relative humidity - on average 45%, ventilation rate - 1.62 m^3 $hour^{-1}$ and chicken.

Three times a week measurements of NH_3 concentration with Draeger Co. Ammonia tubes took place. In the last (5th) growth cycle on the same DL material in chamber 1 and 3 a new measurement technique - multi-gas-monitoring consisting of multi-gas monitor 1302, multipoint sampler 1309, laptop with software 7300 (Bruel & Kjaer, Denmark) - was used. By the help of multi-gas-monitoring it is possible to measure continuously up to 5 different gases. We used ammonia, carbon dioxide and nitrous oxide filters and determined these gases during the whole keeping period in all 3 chambers. On the basis of averages and known ventilation rate emissions of ammonia were calculated. The experimental conditions were described by Hoy and Kühnel (1995).

RESULTS

In straw system weekly means of ammonia were low in the first 4 weeks (between 1 and 9 ppm) and increased in week 5 up to 12 ppm in 1st growth cycle and up to 25 ppm in 5th growth cycle (Fig. 1). This is due to increasing amount of faeces combined with compaction of straw. The consequence was a rising emission active area in the chamber. In both DL systems the same tendency was evident but on a higher level of NH_3 concentration. Already in first keeping week the young chicken met a high ammonia concentration increasing from week to week (weekly means up to 18 ppm with maximum of 29 ppm). This is caused by NH_3 desorption from the depth of DL bedding influenced by high temperature during the first keeping week. After desorption a decrease in ammonia concentration from week 2 to 3, 4 respectively was observed. Weekly means of NH_3 reached in the last keeping week in both DL systems values up to 38 ppm with maximum of 74 ppm (Fig. 1).

Especially during mixing DL material after the end of (last) keeping period a strong increase in ammonia concentration with a peak nearly 100 ppm was observed (Fig. 2). Nearby, it was possible to determine also dynamics of nitrous oxide concentration by the help of multi-gas-monitoring. The emission of N_2O is caused by disturbances in nitrification in DL bed. While in straw keeping system weekly averages of nitrous oxide ranged between 290 and 710 ppb (mean concentration in the atmospheric air 300 to 310 ppb) in deep litter system with mixing the N_2O means were more than 1 ppm (table 1).

During mixing deep litter nitrous oxide concentration reached maximum of appr. 3 ppm (Fig. 2). On the basis of NH_3 measurements emission of ammonia related to keeping system was calculated considering the following parameters: outlet air volume - 162 m^3 $hour^{-1}$, duration of keeping period - 36 days, 8.9 growth cycles per anno and average live weight at the end of fattening period - 1.75 kg. The calculated emission of ammonia was:

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- in deep litter system without mixing: 23.9 kg/500 kg live weight and anno
- in straw system: 13.6 kg/500 kg live weight and anno
- in deep litter system with mixing: 31.0 kg/500 kg live weight and anno.

Table 1: Weekly means of N_2O concentration in dependence on keeping system (ppm)

	Deep litter without mixing	Straw	Deep litter with mixing
Week 1	.69	.29	1.26
Week 2	.84	.20	1.25
Week 3	1.00	.55	1.07
Week 4	1.16	.63	1.01
Week 5	1.32	.71	1.02

Last (5th) growth cycles: means of 340 values per week and chamber.

CONCLUSIONS

1. Deep litter housing of broiler chickens on the basis of wood chips and with additives leads to a high concentration of ammonia during mixing used litter material and especially during first and last week of the following keeping period.

2. Because of high emission of ammonia and less practicability a deep litter system with additives and mixing cannot be recommended.

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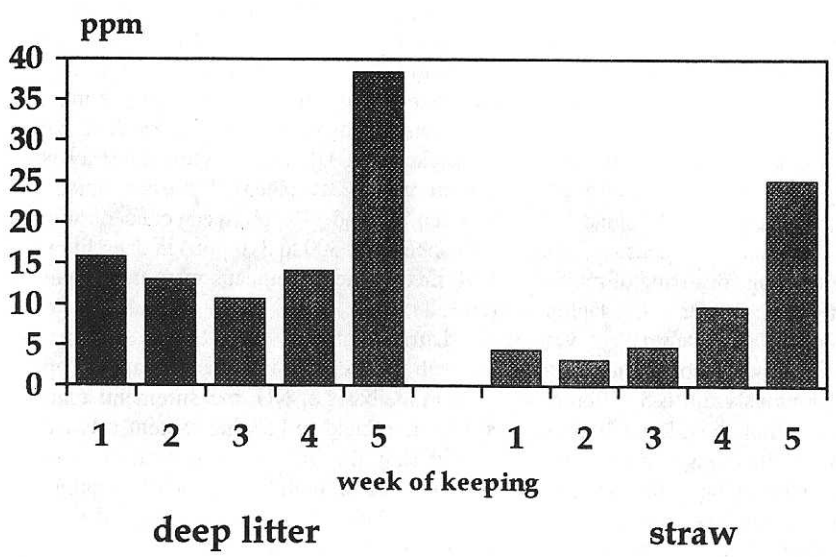

Fig. 1: Mean concentration of ammonia in broiler houses with straw or deep litter (ENVIROZYME-system: with additive and mixing). Averages of keeping weeks - 5th growth cycle.

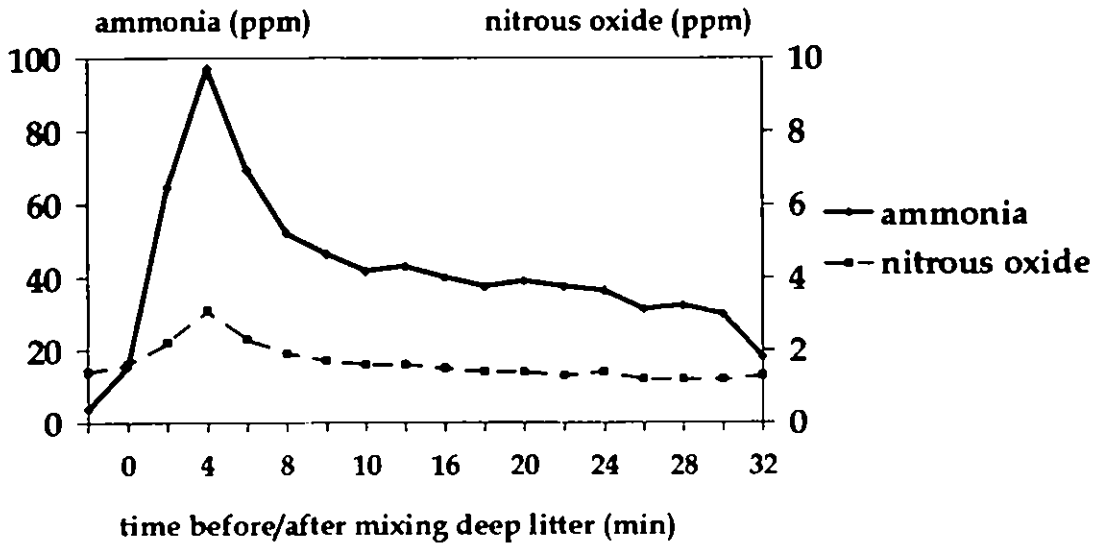

Fig. 2: Dynamics of ammonia and nitrous oxide concentration during mixing of deep litter material at the end of keeping period (5th growth cycle)

THE SPATIAL DISTRIBUTION OF AMMONIA EMISSIONS IN GREAT BRITAIN FOR 1969 AND 1988 ASSESSED USING GIS TECHNIQUES

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Abstract - Maps of ammonia (NH_3) emissions are a key input for models describing the atmospheric transport and deposition of NH_3. An important question is whether emissions have changed over recent decades. There is evidence that total emissions have increased, largely since 1950, but up until now no attempt has been published to quantify the historical changes in spatial distribution of NH_3 emissions for Great Britain. The present paper shows how livestock numbers and crop areas have changed between 1969 and 1988. Using this information in 5 km grid form, together with information on N fertilizer use and livestock emissions, preliminary NH_3 emission maps have been constructed for 1969 and 1988. The results show substantial changes in the sources and patterns of NH_3 emission, related to changing agricultural policies and practice. In particular, there is an increased spatial variation in the emissions in 1988, probably due to larger farm sizes, however, there is currently significant uncertainty in the total magnitude of NH_3 emissions for 1969, due to differences in N input to livestock systems.

1. Introduction

The regional and national distribution of NH_3 emission estimates is of great interest for atmospheric transport modelling and assessing the effects of NH_3 deposition. In principle, measurements of NH_3 concentrations would be the best approach to quantify dry deposition to ecosystems, for comparison with maps of critical loads (e.g. UNDITE 1994). However, the extreme spatial variability of NH_3 emissions and air concentrations would require a very large number of monitoring stations. On a national scale, gridded NH_3 emission inventories, together with application of atmospheric transport models, therefore provide essential tools to quantify the distribution of NH_3 deposition.

The spatial distribution of NH_3 emissions in the UK was estimated first by ApSimon *et al.* (1987) at a 10 km grid for England and Wales, and has been estimated more recently on a 5 km grid for GB by Eager (1992) and Sutton *et al.* (1995). The latter study provided NH_3 emissions for 1988, however effects of nitrogen deposition occur over decades, and the magnitude of past emissions and their distribution are also relevant. The present paper addresses the question of changes in the pattern of NH_3 emissions between 1969 and 1988. It integrates the agricultural emission mapping of Eager (1992) with emissions from non-agricultural sources and the most recent official emission factors (DOE 1995) on a 5 km grid for Great Britain.

Table 1: Total NH_3 emissions in the UK (1993) according to DOE(1995) and equivalent emission factors.

Source category	livestock (thousands)	total emissions (Gg NH_3 yr^{-1})	emission factor (kg NH_3 $animal^{-1}$ yr^{-1})
Cattle & calves	11729.0	160	13.64
Pigs	7753.8	30	3.87
Sheep & lambs	43901.0	20	0.46
Fowls	5453.0	30	0.23
Tillage & cut grass		40	
Non-agric. emissions	-	40	-
Total emissions		320	-

2. Methods

The main data source for spatially disaggregating NH_3 emissions in Britain is the June Agricultural Parish Census of MAFF. Using this information, agricultural emissions were scaled by animal numbers and crop areas, as summarized by MAFF (1973, 1990). These parish data were used in a 5 km grid format according to the reaggregation of Data Library, University of Edinburgh (Hotson 1988). Livestock emissions were scaled by emission factors per animal, and crop emissions derived information on average N application rates to crops (Boyd 1966, Church 1974, Dyer *et al.* 1989) together with an average fractional loss of applied N as NH_3.

Several estimates of NH_3 emissions in the UK have been provided recently (Sutton *et al.* 1995, Pain *et al.* 1995, pers. comm., ApSimon *et al.* 1995, pers. comm.). In the present study, equivalent NH_3 emission factors were derived from the official DOE figures (Table 1).

Non-agricultural sources were largely distributed by human population. The derived emission factors were used to scale the spatial distribution of NH_3 emissions according to 1969 and 1988 distribution. For this paper, the average 1993 emission factors for livestock (Table 1) were used unchanged for the 1969 and 1988 inventories, which is a signifcant source of uncertainty for the 1969 estimates. In contrast, the crop emissions for each year were calculated using data from the Survey of Fertilizer Practicefor the appropriate years (Boyd 1966, Church 1974, Dyer *et al.* 1989). Each of the components was implemented in the GIS system ARC/INFO 6.1 to provide the mapped distribution of emissions.

4. Results and discussion

The figures in Table 1 show that livestock agriculture represents by far the largest source of NH_3 in Great Britain. Hence changes in livestock numbers and distribution will be the main factors affecting the pattern of NH_3 emissions between 1969 and 1988. Changes in the total numbers and demographic structure of livestock between these years are shown in Table 2. The figures indicate that, with the exception of sheep, only relatively small changes in total numbers of livestock have occurred. However, there have been substantial changes in the demographic structure of each of the animal types. For example, there has been a decrease in the fraction of dairy cattle since 1969. This can be related the introduction of milk quotas (1984). Such changes in policy will have affected NH_3 emissions per animal because of the different N excretion from different animal sub-classes.

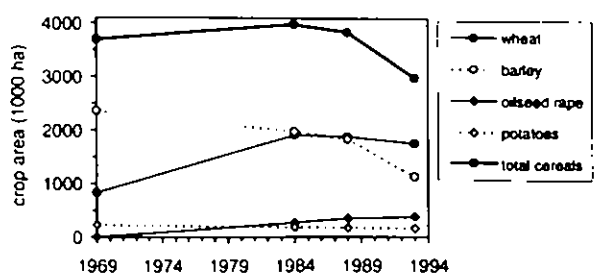

Figure 1: Changes in crop area in Great Britain between 1969 and 1993. Derived from MAFF (1973,1994).

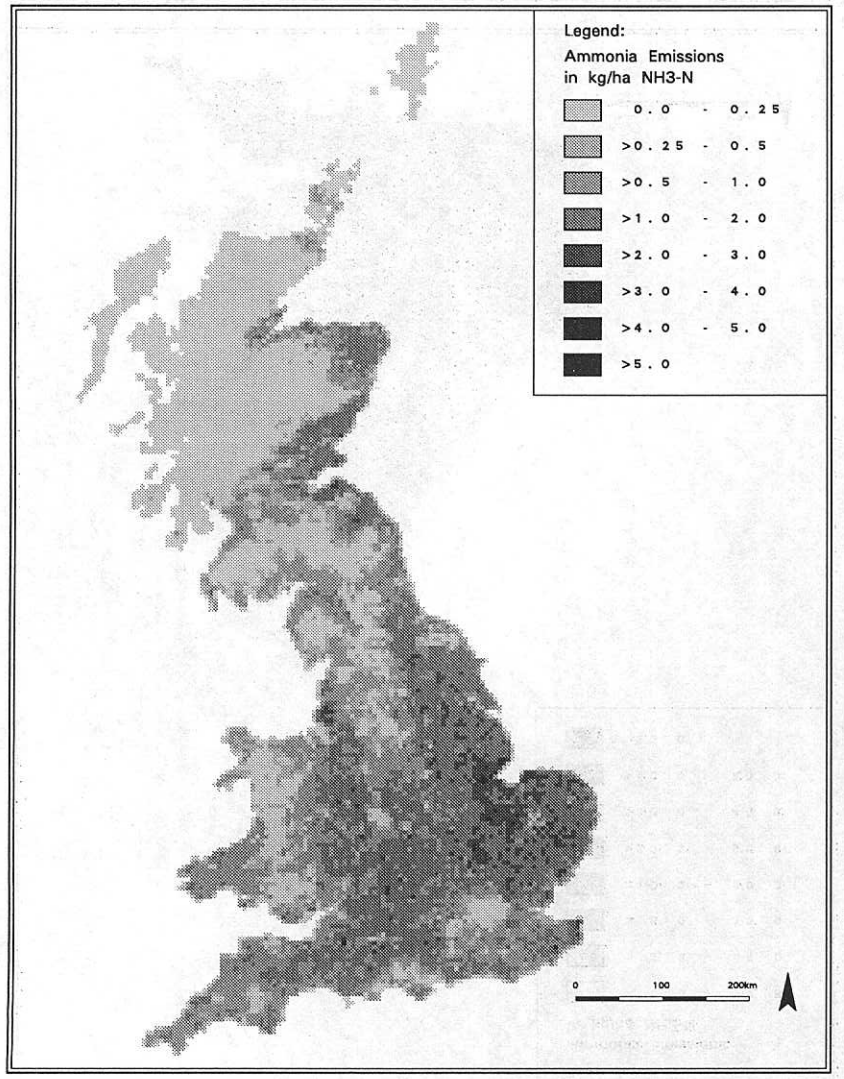

Figure 2. Ammonia emissions from fertiliser application and crops for 1969.

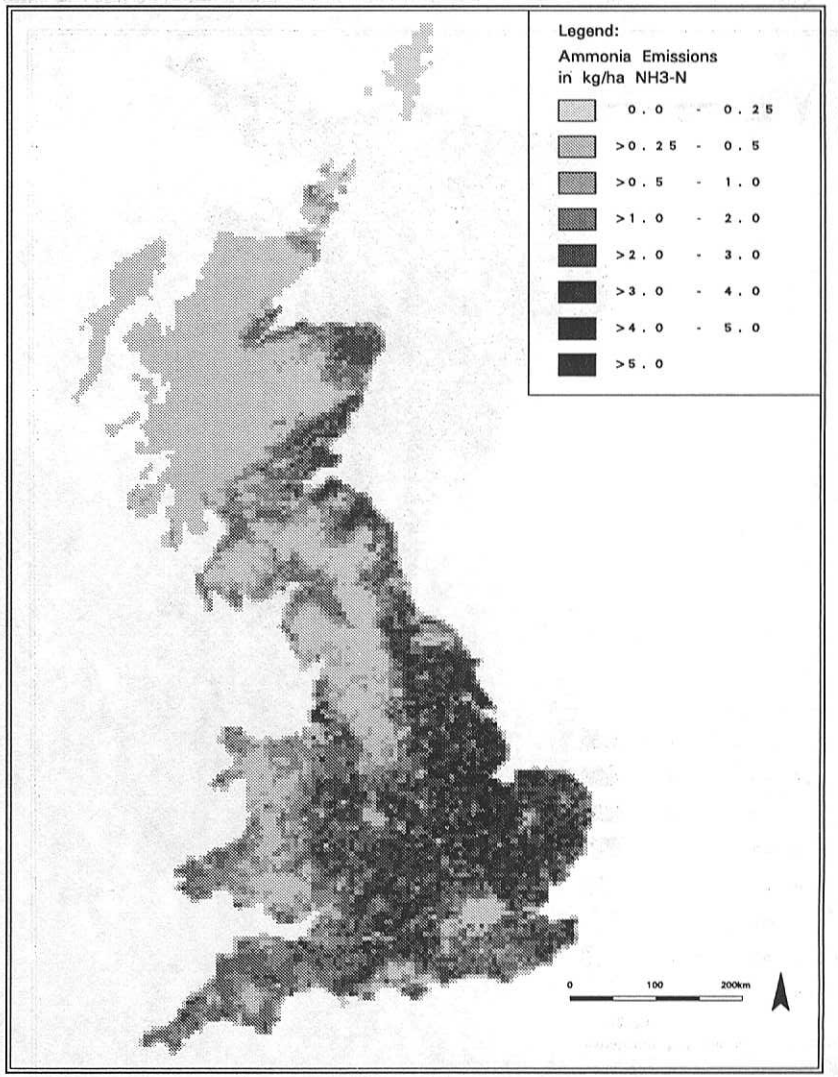

Figure 3. Ammonia emissions from fertiliser application and crops for 1988

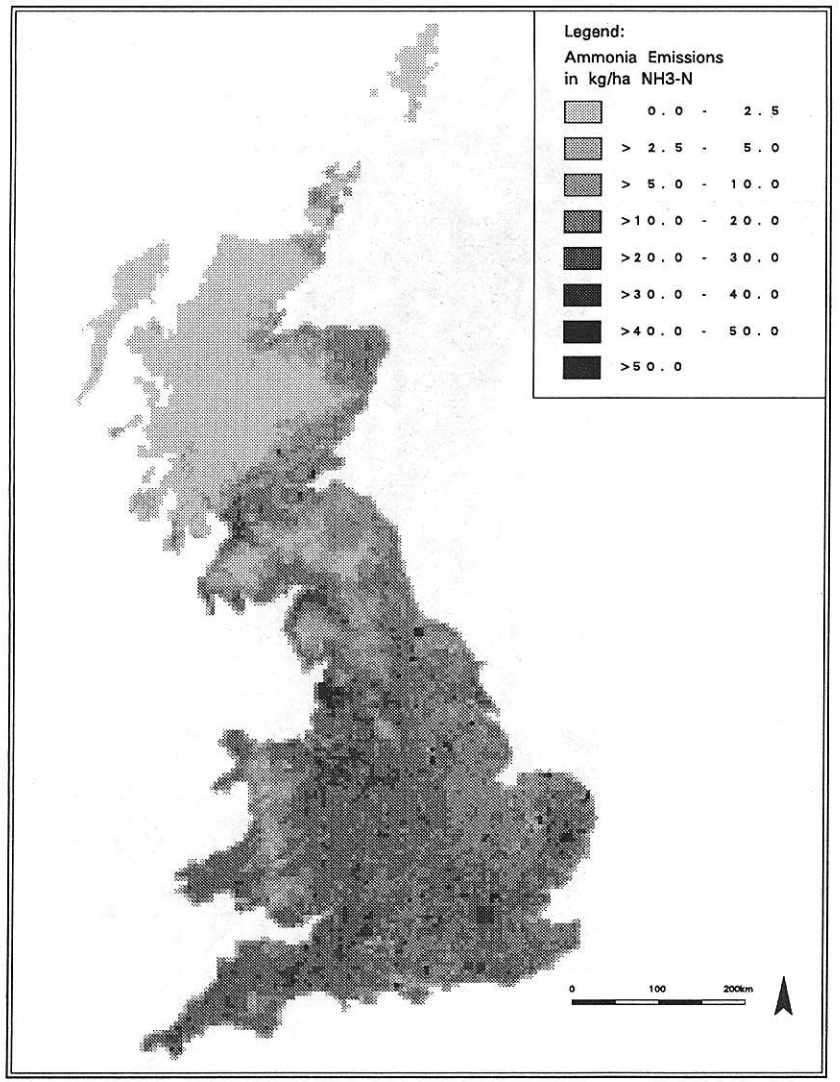

Figure 4. Total NH_3 emissions from agricultural and non-agricultural sources for 1969.

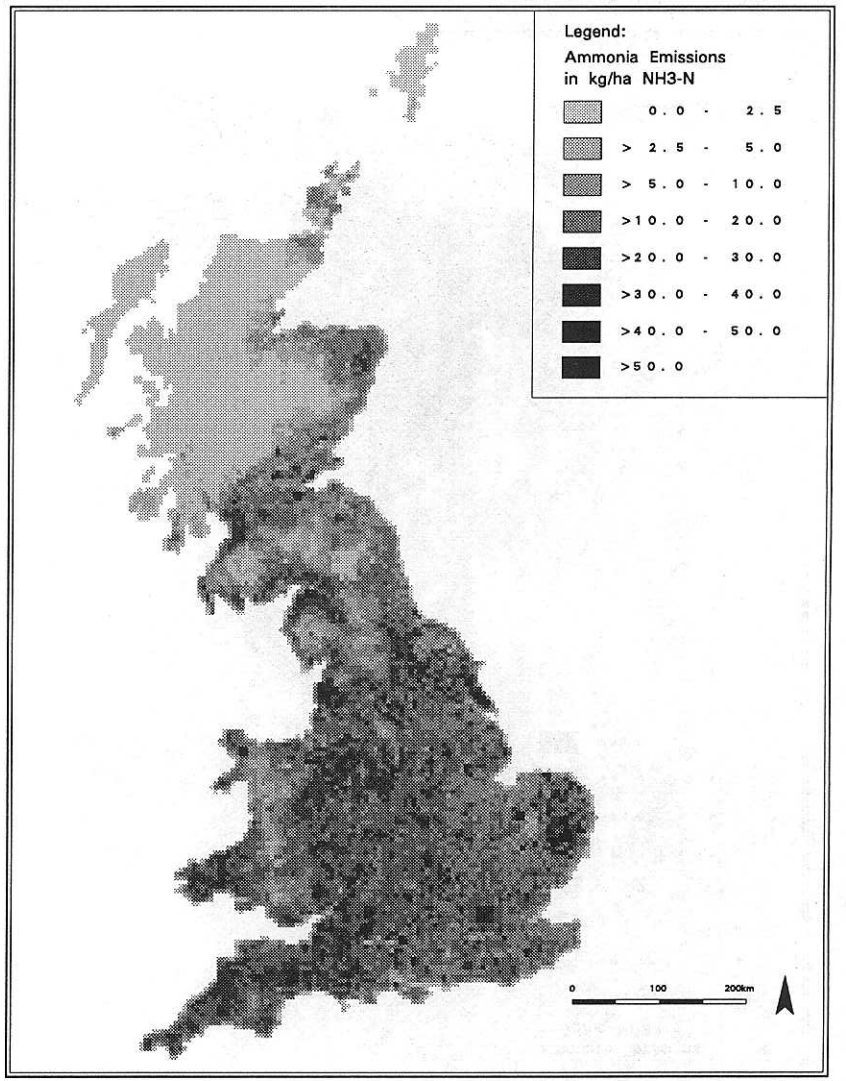

Figure 5. Total NH_3 emissions from agricultural and non-agricultural sources for 1988.

Table 2: Changes in livestock demography 1969-1988

Livestock	Livestock class	Animal numbers (1000s)		% change
		1969	1988	
Cattle	<2 years	2,234	2,747	23
	dairy cattle & calf cattle	4,685	3,662	-22
	bulls	85	48	-44
	fattening calves	1,597	1,627	2
	young fattening cattle	1,477	774	-48
	other cattle > 2 years	1,054	1,496	42
	total	11,132	10,355	-7
Pigs	breeding & other sows	818	805	-2
	boars	41	40	-2
	fattening pigs >50 kg	996	2,351	136
	fattening pigs 20-50 kg	3,048	2,086	-32
	piglets (<20kg)	1,844	2,042	11
	total	6,747	7,324	9
Sheep	ewes	13,711	18,274	33
	rams	327	783	139
	lambs	11,635	19,442	67
	total	25,673	38,512	50
Poultry (Fowls)	laying hens < 18 weeks	53,996	10,326	-81
	laying hens > 18 weeks	11,784	33,931	188
	all hens for breeding	5,626	5,607	0
	cocks & other table fowl	1,636	995	-39
	broilers	35,519	69,460	96
	total	108,561	120,319	11

Ammonia emissions and agricultural policy are closely linked. Asman *et al.* (1988) reported an 81% rise in NH_3 emissions across Europe between 1950 and 1980, which was estimated on the basis of changes in livestock numbers and fertilizer use. However, intensification is also expected to have increased NH_3 emissions per animal, particularly where these are fed grass with increased nitrogen content. These and other changes (changes in demography, animal breeding) make the identification of correct figures for historical livestock NH_3 emissions highly uncertain, and this is the subject of ongoing investigation.

It is clear that agricultural policy has had an increasing influence on farming in Britain. This trend was accentuated since the entry of the UK into the EC (1973), with the subsequent intervention of the Common Agricultural Policy (CAP). In addition to the effects on livestock, direct changes in crop production have also affected NH_3 emission. The areas of the major arable crops under cultivation in Britain over the period 1969-1993 are shown in Figure 1. This shows an increase in area under wheat and oilseed rape, both crops receiving high levels of N fertilizer. In addition, N inputs (kg N ha^{-1} $year^{-1}$) have generally increased over the period (Boyd 1966, Dyer *et al.* 1989). In contrast, the area of barley and of total cereals has decreased since 1988, as a result of CAP changes in response to overproduction of food, resulting in the introduction of 'set aside' (1988).

Examples of the mapped distribution of NH_3 emissions at 5 km x 5 km grid resolution for Great Britain are shown in Figures 2-5. The most dramatic changes have occurred for emissions from fertilizers and crops. Total crop emissions for 1988 are estimated at 43 Gg NH_3 $year^{-1}$ as compared with 32 Gg $year^{-1}$ in 1969, and this comparison is shown in mapped form in Figures 2-3. The change is a result of both changes in crop areas and increase in fertilizer application rate. Total ammonia emissions for 1988 and 1969 are estimated at 300 Gg $year^{-1}$ and 287 Gg $year^{-1}$, respectively. Although this is not a large difference overall, Figures 4 and 5 show how the spatial pattern of NH_3 emissions has changed substantially over the period. In 1988, there is a much larger spatial variability in emissions, probably associated with the increase of larger livestock farms as well as reduced activity on marginal land. This would be expected to have provided an increased impact of local NH_3 emissions in source areas.

It should be noted that the 1969 total emission map (Figure 4) is very largely affected by the contribution of NH_3 emissions from livestock. Given the changes in fertilizer application rates to grassland (and hence to animal feeds), there is considerable uncertainty over the emission factors to be applied, particularly for cattle and sheep. The present values were made using the same emission factors for different years, based on Table 1 for the most recent estimates. For example, although demographic changes would have favoured larger emissions in 1969 for cattle, smaller rates of fertilizer N input probably mean that emissions per animal were significantly smaller at this time. This aspect together with an assessment of the reliability of the spatial disaggregation are both areas requiring further study.

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AMMONIA EMISSIONS IN RUSSIA

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Abstract - An attempt to assess the magnitude of ammonia emission into the atmosphere in Russia from cattle breeding and poultry enterprises of industrial type is made in this work for the first time. The calculations were based on the official statistical data on the total number of cattle and poultry, as well as on emission factors typical for Europe. Ammonia emission due to cattle breeding and poultry in Russia in 1992 is estimated as 1599 Gg NH_3, including 1151 Gg on the European territory of Russia (ETR). Official statistical data on NH_3 emissions from different branches of industry are presented and amounts to 71 Gg. A rough estimate of ammonia emissions from fertiliser use in Russia is 157 Gg. Total ammonia emission in Russia in 1992 is estimated 1827 Gg.

Data on ammonia emissions in agriculture in Russia are presented for the last five years. A certain tendency of decrease in NH_3 emissions is indicated due to decrease of total number of agricultural animals.

Key words: Ammonia emission, industry, cattle-breeding, poultry, nitrogen fertilisers.

Ammonia emission into the atmosphere has received much attention in the last years not only because these compounds (as well as sulphur and nitrogen oxides) contribute to precipitation acidification. After nitrogen and nitrogen oxide, ammonia is the next most widespread nitrogen-containing compound in the atmosphere, and as it has become apparent, its cycle in the environment plays an important role in the natural nitrogen cycle. For instance, calculations of the nitrogen balance on the territory of the former USSR (data for 1986-1987) indicate that about 65% of the total quantity of anthropogenic nitrogen entering the atmosphere is due to ammonia emissions (Artemov *et al.*, 1990).

It should be pointed out that in Russia the problem of atmospheric emissions of ammonia is of current concern not only owing to the increase of the quantity of nitrogen entering the environment. Monitoring data for 73 industrial cities in Russia in 1993 demonstrate that many of these cities are characterized by increased content of ammonia in the atmosphere (Anon. 1994a). It is sufficient to mention that the annual ammonia content in Russian cities in 1993 exceeded maximum permissible concentrations (MPC_{NH3} = 40 $\mu g\ m^{-3}$) and amounted to 44 $\mu g\ m^{-3}$, while maximum 20 minute averaged concentrations reached 1600 $\mu g\ m^{-3}$.

In Russia control over industrial ammonia emissions (see statistical data for 1992 in Table 1 (Anon. 1994b)) is effected on a regular basis, but as to agriculture being the main source of atmospheric emissions of ammonia, it is not taken into consideration. In our previous paper we tried for the first time to calculate ammonia emissions due to cattle-breeding enterprises on the European territory of Russia (ESTR) (Tsibulski *et al.*, 1994). In this work we have extended our investigations to the whole territory of Russia and have considered one more source of ammonia agricultural emissions, namely application of mineral fertilisers. We based our calculations on the data on the head of livestock and poultry bred on industrial basis (Goskomstat, 1994). We used values of emission factors generally accepted in West European conditions (Asman, 1992).

Table 2 summarizes the calculation results for ammonia emissions in Russia for the recent years. There is a clear tendency of ammonia emissions to decrease, though this is due not to emission reduction measures, but to decrease of the total number of animals, which is caused by the economic crisis in Russia.

The second source of ammonia emissions in agriculture is application of organic (manure) and mineral fertilisers. The emission factors which we use to calculate ammonia emissions due to cattle already include ammonia emissions due to application of (organic) fertilisers to soil.

Ammonia emissions caused by application of mineral nitrogen - based fertilisers are determined by many factors such as soil characteristics, ploughing depth, temperature and so on. In the former USSR total losses of nitrogen were estimated on the basis of experimental data as 6% of the fertiliser and N applied (Artemov *et al.*, 1990; 1986). These values are in good agreement with the data (AEIG, 1995); in AEIG (1995) this coefficient for northern areas is estimated as 5%.

Table 1: Official statistical data on ammonia emissions in Russia in 1992.

	Sectors	Emissions Gg NH_3 $year^{-1}$
1	Chemical and petrochemical	34.542
2	Fuel	5.977
3	Food industry	5.093
4	Ferrous metallurgy	4.279
5	Machine building and metal working	3.178
	Non-ferrous metallurgy	
6	Woodworking and wood - pulp and	1.719
7	paper industry	0.995
	Light industry	
8	Medical industry	0.426
9	Microbiological industry	0.383
10	Construction material industry	0.168
11	Transport	0.076
12	Power production	0.030
13	Flour and cereasl industry and animal	0.014
14	formula feed production	0.001
	Total for 14 sectors	**56.880**
	Total for the whole country	**70.983**

Table 2: Ammonia emissions in cattle-breeding and poultry in Russia for the last five years.

Domestic animals	1989		1990		1991		1992		1993	
	Head of livestock, (millions)	NH_3 emission, (Gg)	Head of livestock, (millions)	NH_3 emission, (Gg)	Head of livestock, (millions)	NH_3 emission, (Gg)	Head of livestock, (millions)	NH_3 emission, (Gg)	Head of livestock, (millions)	NH_3 emission, (Gg)
Cattle,	54.3	1250.5	52.1	1200.7	54.7	1260.6	52.2	1202.4	36.3	835.4
incl. on the ETR	43.4	1000.1	41.6	958.6	39.0	898.7	37.1	854.9	26.6	613.4
Pigs,	41.3	221.1	43.6	322.8	34.5	185.0	31.5	169.0	20.3	108.6
incl. on the ETR	30.8	165.0	29.1	155.9	25.6	137.1	23.4	125.4	15.8	84.5
Sheep and goats,	72.8	123.5	57.5	97.6	55.2	93.7	51.3	87.1	40.0	67.9
incl. on the ETR	46.9	79.6	33.8	57.4	40.3	68.4	37.4	63.5	31.6	53.6
Poultry,	660.0	163.7	668.0	165.7	647.6	160.6	568.2	140.9	568.2	140.9
incl on the ETR	606.1	125 3	513.2	127.3	494.8	122.7	432.3	107.2	432.3	107.2
Total		1758.7		1697.8		1670.0		1599.4		1152.7
incl. on the ETR	-	1370.0		1299.1		1227.0	-	1150.9	-	858.7

Table 3 summarizes statistical data on the quantities of nitrogen-based fertilisers supplied to agriculture in Russia for the last four years (Goskomstat, 1995), it also contains data on ammonia emissions calculated on the basis of these quantities.

As in the case of cattle breeding there is a clear tendency of ammonia for decrease due to sharp decrease of application of nitrogen-based mineral fertilisers. Total ammonia emissions in Russia due to industrial and agricultural activity in 1992 are presented in Table 4.

Table 3: Ammonia emissions in Russia under application of nitrogen-base mineral fertilizers.

Years	1990	1991	1992	1993
Supply of nitrogen-based fertilisers to agriculture, (Gg)	4334	3967	2622	2083
NH_3 emissions under application of nitrogen-based fertilisers, (Gg)	260	238	157	125

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Table 4: Total agricultural and industrial emissions of ammonia in Russia in 1992

Sector	NH_3 emissions, Gg
Industry	71
Agriculture: cattle - breeding	1599
Application of fertilisers	157
Total	1827

NITROGEN EMISSIONS IN GERMANY AND POTENTIAL FOR THEIR REDUCTION

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Abstract-Ammonia emissions have been quantified for the Federal Republic of Germany, including the former German Democratic Republic, from 1970 to 1994. In the western part of Germany, annual ammonia emissions ranged from 520 to 590 Gg NH_3 $year^{-1}$. In the former GDR they varied between 220 and 270 Gg and then, as of 1991, decreased sharply to values of less than 110 Gg due to a sharp decline in livestock numbers. Over 90 % of the NH_3 emission originates from agricultural sources. Nevertheless, catalyst equipped vehicles emit substantially more NH_3 than other vehicles, so that with increasing use of catalysts, this source may contribute 10% of the total German NH_3 emission by 2000. Measures to reduce NH_3 emissions centre on the agricultural sources, including practices associated with managing livestock wastes, livestock housing, modified feeding, livestock numbers and fertilizer/nutrient levies.

The compilation presented here includes emissions from the following sources: livestock farming; use of nitrogen-containing fertilisers; industrial processes (ammonia production, production of nitrogen-containing fertilisers, production of calcinated sodium carbonate, low-temperature lignite coking); combustion plants; and DENOXing as well as road transport. It does not take into account the emissions caused by natural processes (e.g. exhalation by humans, microbial activities in soil) as well as from refrigeration equipment (emissions of less than 1 Gg), modes of transportation other than road (not quantifiable at present) and the spreading of sewage sludge. Agriculture is the main source of ammonia emissions (1994: 85.5% from livestock farming, 9.3% from fertiliser use).

As 90% of air-borne gaseous ammonia is transformed in the atmosphere into ammonium compounds within one hour, considerable amounts of ammonia and ammonium can be carried into Germany from other European countries by way of long-range transboundary atmospheric transport, and vice versa. Based on model calculations, the transboundary atmospheric export of reduced nitrogen compounds (NH_4^+ and NH_3) from Germany into other European countries is estimated at approx. 125 Gg N $year^{-1}$ (reference year: 1989), with Poland receiving the greatest share (21%), followed by the former Soviet Union (18%) and the former CSFR (14%). These exports are contrasted by annual imports into Germany of approx 102 Gg N $year^{-1}$ mainly from the Netherlands (27%) and France (27%).

Calculation methodology

The estimates of NH_3 emissions provided were based on reference data from a number of sources, as shown in Table 1, combined with emission factors for each reference parameter (Table 2).

The emission factors shown in Table 2 were obtained from CORINAIR emission factor handbook as well as from investigations conducted by Volkswagen AG.

Table 1: Reference data sources for ammonia emission estimates.

Sector	Reference data	Source
Livestock farming	Statistics on livestock numbers	Federal Statistical Office, Federal Ministry for Food, Agriculture and Forestry
Fertilizer use	Amounts of mineral fertilizers applied annually	Federal Statistical Office
Industrial processes	Production statistics	Federal Statistical Office
Combustion plants	Energy use data	Energy balance prepared by the Arbeitsgemeinschaft Energiebilanzen
DENOX process	Installed capacity	VDEW statistics
Road transport	Number of in-use vehicles, vehicle-kilometres	Federal Ministry of Transport, German Institute of Economic Research

Table 2. Ammonia emission factors applied in this study.

Sector Reference parameters	Emission factor
Livestock farming	kg NH_3 animal^{-1} year^{-1}
Cattle	23.04
Pigs	5.36
Poultry	0.25
Horses	12.20
Sheep	1.70
Fertilizer use	kg NH_3 Mg fertilizer^{-1} 40
Industrial processes	kg NH_3 Mg product^{-1}
Ammonia production	0.8
Mineral fertilizer production	5.0
Low-temperature lignite coking	0.4
Production of calcinated sodium carbonate	7.0
Combustion plants	kg NH_3 TJ^{-1}
Coal	0.14
Lignite	0.60
Natural gas	0.15
Town gas	0.87
Household and industrial waste	14.7
DENOX process	kg NH_3 (Mw installed capacity)$^{-1}$ 36
Road Transport	mg NH_3 km^{-1}
Motorcycles	2
Otto-engine cars	2
Catalyst-equipped otto-engine cars	90
Diesel-engine cars	1
Heavy-duty vehicles	2

CORINAIR emission factor manual. With respect to road transport, Otto-engine motor vehicles equipped with a closed-loop three-way catalyst are the main source, with the emissions generated mainly in operating modes in which the air/fuel ratio deviates from the ideal value (lambda = 1). According to results obtained by Clausthal University, the rate of ammonia formation increases by some 3000% if the excess air coefficient is 2% lower than the ideal value. This means that increased equipment of motor vehicles with closed-loop three-way catalysts will cause ammonia emissions to increase. By the year 2000 it is estimated that this will contribute 10% of the total NH_3 emission! This estimate assumes (i) that the ammonia emissions will be approximately at the same level as present and (ii) that all cars in Germany will be fitted with catalytic converters by the year 2000.

Ammonia as the future main source of nitrogen inputs into the atmosphere

It is of interest to compare the magnitude of nitrogen emissions as nitrogen oxide and ammonia. In 1992 2357 Gg of nitrogen oxide (NO_x as NO_2) were emitted in Germany which corresponds to about 720 kt as nitrogen. In the same year, emissions of nitrogen in ammonia compounds amounted to 535 kt. With NO_x emissions from traffic expected to decrease further due to an increase in the number of vehicles equipped with closed-loop three-way catalytic converters, ammonia emissions are expected to become the main source of atmospheric nitrogen inputs in Germany.

Ammonia emissions in Germany

The contributions of the different sources and total NH_3 emissions for former East and West Germany and the whole of the country are shown in Table 3. In the western part of Germany, annual ammonia emissions ranged from 520 to 590 Gg NH_3 year^{-1}, while in the former GDR, emissions varied between 200 and 270 Gg year^{-1} up to 1990.

The sharp decrease of NH_3 emission in the former GDR from 1990-1994 to emissions of 110 Gg year^{-1} is mostly due to the dramatic reduction in livestock numbers as well as reduced fertilizer use and industrial emissions.

Potential measures to reduce ammonia emissions

As agricultural sources provide most of the NH_3 emission, measures to reduce emissions have focused on these sources. Table 4 lists measures to reduce NH_3 emissions effectively in Germany.

Table 3. Overview of NH_3 emissions in Germany

	Livestock farming			Fertiliser use			Industrial processes			Combustion plant			Emissions other sources			Total emission		
	West	East	Total	West	East	Total	West	East	Total	West	East	Total	West	East	Total	West	East	Total
Values expressed as Gg NH_3 $year^{-1}$																		
1970	466	187	652	45	20	66	10	9	19	2	2	4	0	0	1	523	218	741
1975	469	205	674	49	27	76	9	11	20	3	2	4		0		530	245	775
1980	497	218	715	62	30	92	9	13	22	3	2	5		0		572	263	835
1985	516	222	738	61	31	91	8	14	22	3	2	5		0		588	269	857
1990	481	173	654	55	20	75	6	10	17	4	2	5	8	0	8	554	205	759
1992	455	97	552	51	13	64	5	5	10	4		5	15	3	17	530	118	648
1994	443	89	533	50	8	58	5	3	8	4	1	5	15	4	19	518	105	623
Values expressed as % contribution to totals																		
1970	89.0	85.7	88.0	8.6	9.4	8.9	1.8	4.2	2.5	0.4	0.7	0.5	0.1	0.0	0.1	100	100	100
1975	88.4	83.8	87.0	9.3	11.1	9.8	1.7	4.4	2.6	0.5	0.7	0.5	0.1	0.0	0.1	100	100	100
1980	86.9	82.9	85.6	10.8	11.4	11.0	1.6	4.9	2.7	0.5	0.7	0.6	0.1	0.0	0.1	100	100	100
1985	87.7	82.5	86.1	10.3	11.5	10.7	1.3	5.2	2.5	0.6	0.8	0.6	0.1	0.0	0.1	100	100	100
1990	86.9	84.3	86.2	9.9	9.8	9.8	1.2	5.1	2.2	0.7	0.8	0.7	1.5	0.0	1.1	100	100	100
1992	85.9	82.1	85.2	9.7	10.9	9.9	1.0	4.0	1.5	0.7	0.9	0.7	2.7	2.1	2.6	100	100	100
1994	85.7	84.9	85.5	9.7	7.6	9.3	1.0	3.2	1.3	0.7	1.0	0.8	3.0	3.3	3.0	100	100	100

Emissions from industrial processes: ammonia production, nitrogen fertiliser production, low-temperature lignite coking, production of calcinated sodium carbonate.

Emissions from other sources: DENOX process, road transport

Data for 1991 and subsequent years are based in part on estimated statistical data.

Table 4. Potential for reducing NH_3 emissions from agriculture.

	Measures			Source-related reduction
1.	Application and storage of farm manure (UBA/LAI, 1994):			
	- time of application, weather conditions			35.0%
	- working liquid manure into soil as soon as applied			
	-- grassland, at least:			50.0%
	-- arable land, at least:			80.0%
	- ground-level application techniques			
	-- band spreading			35.0%
	-- sliding shoe spreading			65.0%
	-- deep and shallow injection			90.0%
	- storage of farm manure (UBA/LAI 1994)		min.	75.0%
			max.	98.0%
	- use of more efficient methods to collect, store and use farm manure (Isermann, 1994)			
	Animal housing construction and technology (UBA/LAI, 1994)		up to	50.0%
	Demand- and productivity-orientated feeding:			
	- minimum (UBA/LAI, 1994)			10.0%
	- maximum (Isermann, 1994)			
	- cattle, maximum (LAI, 1993)			24.0%
	- pigs, maximum (LAI, 1993)			40.0%
	Area-related limitation of livestock numbers			
	Reducing livestock numbers to 0.6 livestock units (LU) per hectare in the spirit of sustainable animal production (present level: 0.91 LU/ha; Isermann, 1994)			34.1%
6.	Levying a fertilizer charge on mineral N fertilizer according to quantity, site and type of farm (Weinschenke, 1989)		min.	8.0%
			max.	36.0%
	Levying a nutrient charge on organic and mineral fertilizer (Becker, 1992)		min	22.3%
			max	30.5%
8.	Replacing mineral fertilizers with organic residues (Isermann, 1994)			
9.	Demand-oriented and well-balanced (50/50) supply of animal and plant protein to the population while simultaneously reducing agricultural exports (Isermann, 1994)			

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Some aspects of ammonia concentrations in the Netherlands

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Abstract

The levels of annual mean ammonia concentrations and their development in time are presented for background, moderate and high-emission areas in the Netherlands. After their spatial representativity was determined, the measured concentrations were compared to calculated concentrations. Lastly, the diurnal and seasonal variations of the measured concentrations are discussed.

INTRODUCTION

Acidification is one of the major environmental problems in the Netherlands. Due to intensive live-stock breeding, the emission of ammonia from manure is one of the dominant contributing sources. For 1993 it is estimated that this source contributes about 45% to the acidic deposition (Erisman & Bleeker, 1995).

To protect vegetation from adverse effects the Dutch government has set limitations to the deposition of potential acid (VROM, 1989). Yearly the Dutch National Institute for Public Health and Environment has to provide the government with estimates of the acidic deposition. The wet deposition field is directly derived from the concentrations in precipitation collected at the 14 sites of the precipitation chemistry network, followed by spatial interpolation. For the dry deposition of SO_x and NO_y the inference method is applied. From the concentrations measured at some 25 stations of the Air Quality Network, the concentration field is obtained by interpolation and this field is subsequently multiplied with the appropriate deposition velocity (Erisman, 1993). For ammonia a different approach is followed. Due to the very high gradients in ammonia concentrations, deriving the concentration field from measurements alone would require a very dense network. Consequently, a combination of measuring and modelling is used. Concentrations for the measurement locations are calculated with the OPS model (Asman & van Jaarsveld, 1992). Subsequently, the emission input data are calibrated such that a best fit is obtained between calculated and measured concentrations. The OPS model is next applied to calculate deposition for the whole receptor area (spatial resolution 5 by 5 km).

This presentation will deal with the level of the ammonia concentrations measured in the Netherlands, the development of concentrations since 1992, their seasonal and diurnal variation and their spatial representativity. Lastly, the agreement with model calculations, both with respect to absolute levels and with respect to diurnal variations, will be presented. The calibration procedure and the results of its application have been described elsewhere (Aben *et al.*, 1995).

MATERIALS AND METHODS

The monitoring network for NH_3

The monitoring network for NH_3 was established in 1992. It consists of 8 stations where the concentration is measured continuously using an annular denuder system (van Elzakker *et al.*, 1995). Three of these stations are located in areas with high emission densities, reaching values of up to about 30 t km^{-2} y^{-1}. The other stations are located in regions with low to moderate emissions.

Measurements for representativity

In order to determine the spatial representativity of the (annual) NH_3 concentrations, measurements with a mobile monitor were carried out around the fixed points. The number of reference points was dependent on the emissions in the surrounding area, decreasing from 8 in high-emission areas, via 6 in moderate emission areas to 4 in background areas. All reference points related to a certain fixed point were sampled at the same day during 15-20 minutes. Before the beginning of a reference measurement, the fixed point was sampled both by the station monitor and the reference monitor to determine systematic differences between both monitors. The reference measurements were repeated several times throughout the year, the number of repeats being dependent on the emission strength in the surrounding area.

RESULTS

Annual mean ammonia concentration

To make maximum use of the measurements obtained, the annual mean is calculated for the September/August period. Table 1 lists some summary statistics based on hourly values from September 1994 to August 1995. The differences between the levels at the respective stations agree reasonably with the initial classification based on estimates of emissions in the surrounding area.

Table 1: Summary statistics of hourly ammonia concentrations for the period September 1994 up to and including August 1995.

station	annual mean	50 percentile	98 percentile	maximum value
131	19.9	12.6	84.6	192
235	3.1	1.7	14.8	36.2
444	1.7	0.5	10.1	31.2
538	4.0	2.3	17.9	214
633	10.6	7.0	44.5	358
722	11.2	8.8	37.5	106
738	18.5	10.5	92.9	499
928	2.3	1.6	8.7	38.7

Development in time

To decrease the deposition of potential acid, measures have been taken to reduce the emission of ammonia. Among these are reduction of emission from storage and application of manure. The total emission of ammonia is reported to have been decreased by about 10% since 1992. Figure 1 shows the development of the mean ammonia concentration for the

September/August period. Except for Station 738, there is no evidence yet for a decrease in the annual mean concentrations. More detailed studies must elucidate whether the reported reduction in emissions can be detected by the measurements, taking into account the influence of meteorological conditions. The decrease observed for Station 738 is probably due to the relocation of this station in the period August '93/September '94.

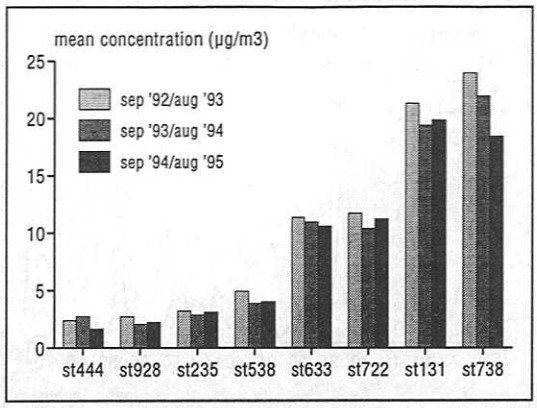

Figure 1: Development of mean ammonia concentrations.

Representativity of measurement locations

For comparison with model results measured concentrations must be interpreted as applying to the whole 5 by 5 km grid cell. Within the 5 by 5 km grid surrounding the fixed measurement point, large variations in the ammonia concentrations occur at a certain point of time, especially in areas with high emission densities (not shown). However, because comparisons between calculated and measured concentrations are done for concentrations averaged for a certain period of time, the mean of all representativity measurements, together with the mean of the simultaneous measurements on the fixed point, is depicted in Figure 2. Also indicated is the standard error of the mean. Clearly, from these measurements there is no evidence for the fixed points not being representative.

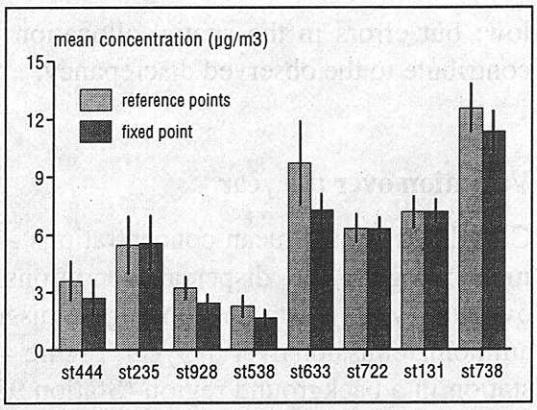

Figure 2: Mean (± 1 SE) of reference measurements and simultaneous measurements at the fixed point.

Comparison with calculated concentrations

Calculated annual mean concentrations, based on estimates of ammonia emissions, show fairly good correlation with measured concentrations (Figure 3). However, especially for stations in high emission areas, the calculated concentrations are much lower than the measured concentrations. Because the concentrations at these stations are determined to a large extent (>90%) by the emissions in the surrounding area (with a radius of 25 km around the station), as is shown by model calculations, this indicates that the estimates for the surrounding area may be too

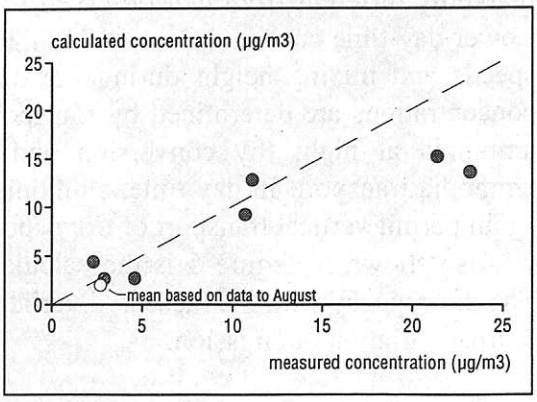

Figure 3: Comparison of calculated and measured annual mean ammonia concentrations for 1993.

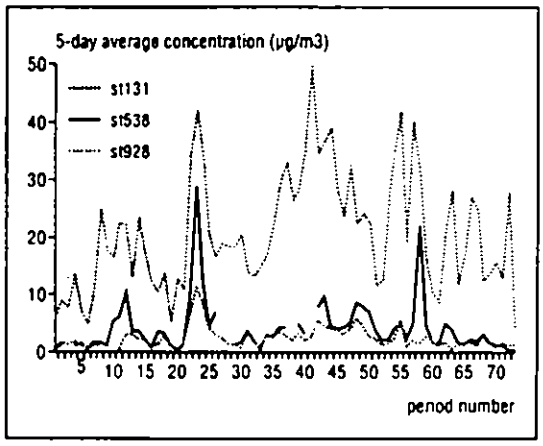

Figure 4: Variation of 5-day average ammonia concentration over the year (1994).

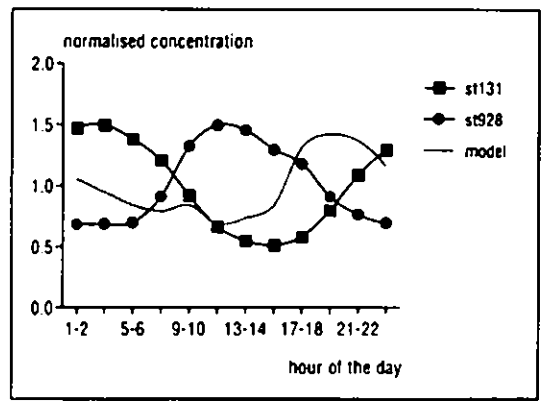

Figure 5: Measured and calculated diurnal variation of hourly ammonia concentrations, averaged over the year.

low; but errors in the spatial allocation of the emissions in the surrounding area may also contribute to the observed discrepancy.

Variation over the year

Calculated annual mean concentrations are sensitive to the interaction between emission and meteorological, i.e. dispersal, conditions. Data on the variation of ammonia concentrations over the year at stations in high-emission areas may be used to derive the variation of ammonia emission over the year. Figure 4 shows this variation, based on 5-day-averages, for a station in a background region (Station 928), a station in a moderate emission region (Station 538) and a station in a high emission region (Station 131). Applications of manure in spring and autumn are clearly distinguishable, especially for Station 538.

Diurnal variation

Calculated concentrations are also sensitive to the interaction between the diurnal variation of emission and dispersal conditions. The diurnal variation of emission at a background station is markedly different from that observed for a high-emission station, as is shown in Figure 5. Lower day-time concentrations at the high-emission station are explained by the higher wind speeds and mixing height during the day. The pattern for the background station, where concentrations are determined by transport from emission areas, is explained by removal of ammonia at night (by conversion and deposition) when atmospheric conditions hinder ammonia transport. In day-time, ammonia concentrations increase as atmospheric conditions again permit vertical transport of tropospheric ammonia.

Also shown in Figure 5 is the calculated diurnal variation for the high-emission station. The discrepancy with the measured variation indicates the need for further investigation of the diurnal variation of emission.

SUMMARY

The ammonia concentrations and their development in time are presented for stations in background to high-emission areas. The reported reduction in ammonia emission in the Netherlands is not yet reflected in the measured concentrations, possibly due to the influence of year-to-year variability in meteorological conditions.

Calculated annual mean concentrations, based on emission estimates, agree reasonably well with measured concentrations. For stations in high-emission areas, however, the calculated concentrations are much lower, indicating underestimation of the emissions in the surrounding area.

Background stations and stations in emission areas show distinctly different diurnal variations of concentrations. The calculated diurnal variation of concentrations for stations in high-emission areas, determined among others by the assumed diurnal variation in emission, does not agree with the measured diurnal variation. This indicates the need for further investigation of the diurnal variation of emission, as the latter may influence the calculated annual mean concentration considerably.

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THE TEMPORAL AND SPATIAL BEHAVIOUR OF NITROGEN CONTAINING AEROSOL AND GASES AND THE CONTRIBUTION TO AMMONIUM AND NITRATE IN RAIN WATER

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ABSTRACT

As part of the UK government's research programme into the phenomenon of acid rain, the composition of collected rain water, ambient gases and aerosols have been made at several locations through out the United Kingdom since 1986 (RGAR, 1990). Results from these measurements, which provide insight into the behaviour of ammonia in the atmosphere are presented.

The total reduced and oxidised nitrogen concentrations in both the gaseous and particulate phases have been determined at two sites in the United Kingdom, Eskdalemuir in Ayrshire and High Muffles on the North Yorkshire Moors, since 1987. The sites are in rural locations where the empirical critical load for nitrogen, assuming the land coverage to be a mixture of moorland and managed coniferous, is in the range 15 to 20 kg N ha^{-1} $yr.^{-1}$.

Comparison of these loads with current estimates of total nitrogen deposition of 22 kg N ha^{-1} yr^{-1} and 19 kg N ha^{-1} yr^{-1} at Eskdalemuir and High Muffles, respectively, show that the critical load limits may be exceeded at both sites. Measured wet nitrogen deposition (based on the 5 km Meteorological Office rainfall values) show that approximately three quarters of the nitrogen deposited is as wet deposition.

Results for the sum of nitrogen contained within both the gaseous and particulate phases have shown that concentrations are highest when the air masses have originated from the southern and eastern wind sectors. The chemical and physical processes leading to the measured concentrations are examined using a trajectory model.

Key word index: Ammonium, wet deposition, aerosol, sector plots.

INTRODUCTION

Results from the UK acid rain monitoring network, will allow further understanding of the removal of ammonia and reactions of ammonia in the atmosphere. This paper will detail information regarding:

* the spatial variability in rain water ammonium concentration and wet ammonium deposition
* trends in secondary particulate matter concentration formed as a result of the presence of ammonia
* origin of secondary pollutants impacting at each of two sampling sites.
* comparison of "nitrogen" concentrations in the aqueous, particulate and gaseous phases.
* comparison of daily measured particulate matter concentration with modelled values.

THE SAMPLING SITES

The two sampling sites discussed in detail; Eskdalemuir and High Muffles, are part of the United Kingdoms "primary" acid deposition network. In addition to monitoring rain water concentrations, a wide range of pollutant are measured; including ozone, sulphur dioxide, nitrogen dioxide and particulate matter. Site characteristics are given in Table 1.

SPATIAL PATTERNS

From 32 weekly bulk precipitation collectors situated in rural locations throughout the United Kingdom, estimates of the concentration of ammonium in rain water are obtained. The 1992 concentration map is presented in Figure 1a. These concentrations are then multiplied by the appropriate 5 km rain fall value, obtained from the Meteorological Office, to obtain an "uncorrected" annual deposition map. However, to account for increased deposition on higher ground due to seeder feeder enhancement (Dore *et al.*, 1992) an additional deposition component is added. The 1992 wet deposition map is presented in Figure 1b. The maps show those areas with high ammonium concentrations; Lincolnshire, southern central England and western central England. These regions are

Table 1. High Muffles and Eskdalemuir sampling site characteristics

	High Muffles	Eskdalemuir
Location	North Yorkshire Moors	Ayrshire
Grid Reference	SE 776939	NT 235050
20 km square	4700 4900	3300 6100
Annual precipitation range for 1986 to 1993 (mm)*	599-947	1275-1528
Estimated wet nitrate deposition to 20 km grid square (N kg ha^{-1} $year^{-1}$)**	5.58	7.58
Estimated dry NO_2 deposition to 20 km grid square (N kg ha^{-1} $year^{-1}$)**	2.38	0.71
Estimated wet ammonium deposition to 20 km grid square (N kg ha^{-1} $year^{-1}$)**	7.56	7.49
Estimated dry ammonium deposition to 20 km grid square (N kg ha^{-1} $year^{-1}$)**	3.31	5.18
Total nitrogen deposition (N kg ha^{-1} $year^{-1}$)	18.83	21.96

* As determined using the bulk precipitation collector
**R.I. Smith, personal communication.

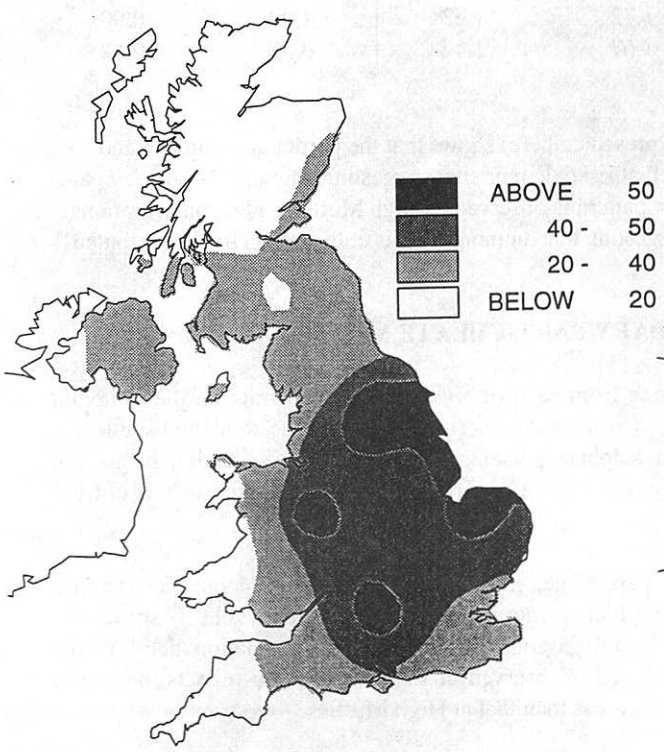

Figure 1a: 1992 Precipitation weighted ammonium mean concentrations (μeq l^{-1})

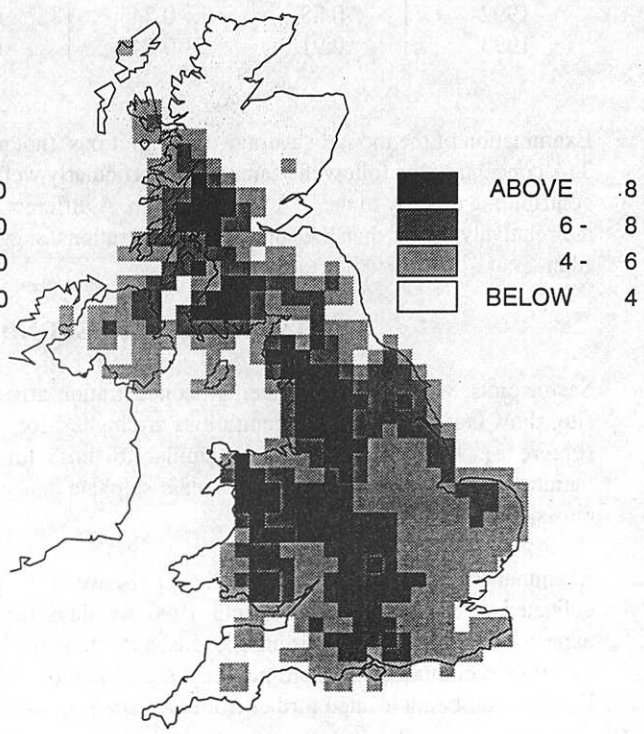

Figure 1b: 1992 ammonium wet deposition (kg N ha^{-1} $year^{-1}$)

characterised by low annual rainfall and the presence of intensive agricultural practices. Conversely, the highest deposition amounts are obtained in areas of high rainfall, indicating the dominating effect of rainwater volume on wet deposition

GASEOUS AND PARTICULATE MATTER CONCENTRATIONS

The total inorganic ammonium (TIA) and nitrate nitrogen (TIN) species are collected using impregnated cellulose filters; citric acid and sodium hydroxide for TIA and TIN, respectively. These measurements are carried out daily and provide input to the modelling studies carried out by EMEP. Sulphate particulate concentrations, determined by collection on washed cellulose filters and subsequent analysis using x-ray fluorescence, are also measured daily. Table 2 presents the mean and median TIN, TIA and particulate sulphate concentrations. Lower concentrations for each species are determined for Eskdalemuir, reflecting the much greater distance of the sampling site from emission sources. Highest concentrations were determined for 1991, a consequence of the relatively low precipitation amounts recorded (626 and 1248 mm for High Muffles and Eskdalemuir, respectively).

Table 2.
Mean and median TIN, TIA and particulate sulphate concentrations recorded at Eskdalemuir and High Muffles

	TIN $\mu g\ m^{-3}$		TIA $\mu g\ m^{-3}$		Particulate sulphate $\mu g\ m^{-3}$	
Eskdalemuir	Mean	Median	Mean	Median	Mean	Median
1989	0.32	0.17	0.77	0.42	1.07	0.67
1990	0.36	0.19	0.92	0.57	0.93	0.59
1991	0.55	0.26	1.27	0.74	1.08	0.73
1992	0.40	0.18	1.09	0.54	0.72	0.44
1993	0.46	0.23	0.93	0.53	0.79	0.51
High Muffles	Mean	Median	Mean	Median	Mean	Median
1988	0.47	0.28	0.78	0.61	1.64	1.34
1989	0.65	0.45	1.44	1.09	1.64	1.26
1990	0.75	0.49	2.05	1.58	1.33	0.97
1991	1.09	0.72	2.51	1.80	1.41	1.01
1992	0.88	0.54	1.72	1.33	1.09	0.90
1993	0.91	0.54	1.67	1.13	0.97	0.68

Examination of the monthly average concentrations (not presented here) shows that the particulate sulphate and TIA concentrations follow the same trend particularly well at Eskdalemuir site, suggesting ammonia is not contributing directly to the TIA concentration. A different pattern is observed at High Muffles; TIA concentrations are relatively higher than the sulphate concentrations, suggesting that ammonia gas is collected on the impregnated filter.

SPATIAL ORIGIN OF SECONDARY PARTICULATE MATTER

Sector plots, which show the average concentration arising from each of eight sectors impacting on the sampling site, show that the aerosol concentrations are highest for wind trajectories originating from the south and south east (Figure 2). These sector plots are similar to those for sulphate presented in RGAR (1990) and indicate that variations in the TIN, TIA and particulate sulphate concentrations are governed by similar factors, such as upwind emission and length of dry periods.

Examination of the correlation coefficients between the particulate, gaseous and deposition amounts for samples collected at Eskdalemuir throughout 1990 for days for which precipitation was collected (Table 3) shows the expected association of ions in the gaseous, particulate and gaseous phases. Greater association between the constituent components of the particulate and gaseous phases is observed at Eskdalemuir and reflects the site at Eskdalemuir being located further from primary SO_2 source areas than that at High Muffles.

Figure 2a. Sector plot of total inorganic ammonium concentrations (μg N m^{-3}) determined 1990-1994

Figure 2b. Sector plot of total inorganic nitrate concentration (μg N m^{-3}) determined for 1990-1994

Table 3. Correlation coefficients between measured concentrations, rainfall and deposition amounts for samples collected at Eskdalemuir throughout 1990 (expressed as a percentage value)

Eskdalemuir	aerosol SO_4	TIN	TIA	SO4 rain	NO3 rain	NH4 rain	Rain	SO_2	Dep. S	Dep. N-N4
aerosol SO_4	100									
TIN	76	100								
TIA	85	87	100							
SO4 rain				100						
NO3 rain	59	51		79	100					
NH4 rain	58		50	76	79	100				
Rain							100			
SO_2	67	66	67					100		
Dep S							63		100	
Dep N-N4									75	100

Note: Only correlation coefficients greater than 50 % are presented

MODELLED TIN AND TIA CONCENTRATIONS

Daily concentrations of both TIN and TIA concentrations were estimated using a trajectory box model (Hackman and Stedman, 1992). Concentrations were estimated by applying the chemical scheme presented by Metcalfe *et al.*, (1989) to a parcel of air transported along daily 96 hour trajectories calculated by EMEP.

Both measured and modelled TIN concentrations determined at Eskdalemuir during 1993 are expressed as a thirty day running mean in Figure 3.

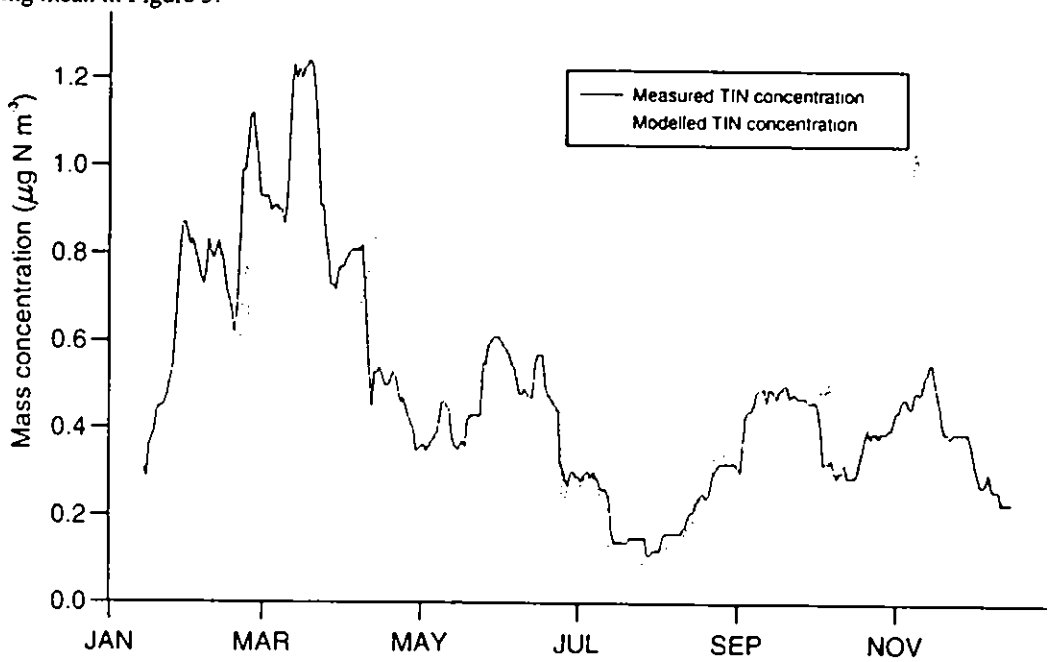

Figure 3. Measured and modelled TIN concentration at Eskdalemuir during 1993

While the annual modelled measured concentrations are within 25 % of the measured values, the temporal variation is not accurately reproduced. This is not surprising given the simple meteorology in the model. There are, however, elements of the month to month variation that are predicted by the model, for example, the small concentrations at Eskdalemuir associated with the persistent westerly flow in July.

SUMMARY

Most of the ammonium wet deposited at each site has originated from the washout of ammonium sulphate and ammonium nitrate aerosol, as indicated from the high correlation coefficients in the aqueous, gaseous and particulate phases and the sector plots showing high concentrations for those sectors arising from southern and southern eastern locations; areas typical of polluted air masses.

Typical ammonia mean concentrations at each site are expected to be in the range 2-3 ppb (RGAR, 1990). When land coverage type is taken into consideration to define the correct rate of ammonia dry removal, approximately 20 % of the total nitrogen input arises from the dry deposition of ammonia gas.

ACKNOWLEDGEMENT

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THE MODEL INVESTIGATION OF ACID COMPOUNDS EMISSION REDUCTION INFLUENCE ON AIRBORNE TRANSPORT AND DEPOSITION OF AMMONIA AND AMMONIUM

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Abstract - Current activity aimed at emission reduction of acidic compounds will result in significant decreasing of sulphur masses in troposphere. In view of current knowledge ammonia air chemistry significantly depends on sulphur compounds. To investigate the influence of sulphur and oxidised nitrogen emission reduction to ammonia and ammonium dispersion over the Europe a special studies were carried out with MSC-E current model. Chemical unit of the model includes chemistry of SO_x , NO_x , NH_x compounds. Deposition fields were calculated for 8 years (1987-1994) using the emission data of SO_2 , NO_2 , NH_3 for 1990. In order to eliminate the meteorological uncertainties the results were averaged and finally map of NH_4^+ deposition was compiled. There were several runs of the model with different emissions for sulphur and nitrogen oxides (e.g. 50% or 1% of SO_2 emission in 1990). Following the same procedure the other maps of ammonium deposition were compiled. Comparison of maps shows that in general there are rather small redistribution of ammonium deposition. At the same time in some regions there is a considerable variation, in particular an increase of deposition was observed in the Mediterranean and Black Sea areas and in Scandinavian countries.

Key word index: acidification, eutrofication, air pollution modelling

INTRODUCTION

In view of current ideas atmospheric transport conditions of ammonia and ammonium are strongly dependent on the availability of acidic compounds - sulphur and oxidised nitrogen compounds [*Finlayson-Pitts and Pitts, 1986*]. Current activities in Europe result in substantial decrease of European sulphur emission from 50 Mt SO_2 in 1980 down to 35 Mt in 1990. Second protocol signed by parties of Convention on Long-Range Transboundary Air Pollution implies further emission reduction down to 23 Mt SO_2 by 2000 year. Such drastic reduction will lead to change of atmospheric consistence which on its term may result in change of distribution of other substance like NH_x. The model experiment aimed at investigation of influence of acidic compounds emission reduction to atmospheric transport of ammonium and ammonia is discussed in this paper.

DESCRIPTION OF THE MODEL EXPERIMENT

The MCS-E operational model for acidic deposition calculations was used in the experiment. Description of the first version of the model is presented in [*Pressman et al, 1991*]. Later chemical scheme was improved

on the basis of [*Finlayson-Pitts, and Pitts, 1986*] and [*Simpson, 1995*].

Meteorological information used in the model is prepared in Russian Hydrometcentre on the basis of numerical short-term weather prediction model. Time interval is 6 hours, resolution is 150×150 km^2.

The influence of underlying surface type and state to dry deposition velocity is calculated for each pollutant separately. Cloud and subcloud scavenging are splitted as well. Precipitation type (snow, rain) and their intensity are also taken into account.

Model experiment includes 4 steps. Each step is characterised by prescribed emission of sulphur and nitrogen oxides in Europe (Table 1). The emission of ammonium was taken as 7926 kt N (official data for Europe). Spatial distribution was also fixed for all compounds (excluding step 2 where distribution for SO_x was taken from IIASA A5 scenario [*Amann et al (1993)*]).

Table 1 Characteristics and results of the experiment

Steps	SO_x emis., kt S	NO_x emis. kt N	NH_x deposition within the EMEP grid, 100 t N	NH_x transport outside the EMEP grid, 100 t N	NH_3 emission - deposition correlation
1) Reference step	19908	6996	71755	7576	0.871
2) IIASA A5 scenario	11160	6996	71701	7626	0.876
3) 1% of SO_x emission	199	6996	71880	7450	0.883
4) 1% of SO_x and NO_x emission	199	70	71426	7912	0.893

At each step 8-years calculations for Europe were carried out followed by averaging of obtained results. It eliminates the year-to-year deviations caused by meteorological variations. Then maps of difference (absolute and relative) between reference map and others were calculated.

For integrated assessment of deposition pattern three parameters were used: amount of ammonium deposited within the grid, amount of NH_x transported outside the grid, and correlation coefficient between ammonia emission and deposition fields.

EXPERIMENT RESULTS AND DISCUSSION.

On the whole there are two contradiction trends (See Table 1 and Figure 1 - Figure 3).

There is an increase of local depositions which is highlighted by the increasing of emission-deposition correlation coefficient. Lower acidic emission causes higher local depositions which is in agreement with theoretical ideas. Dry deposition velocity of ammonia is higher than ammonium one which is the most important

near the source. So, there is an obvious consequence: reduction of acidic emission → lack of oxidants near the ammonia sources → increase of ammonia concentration → increase of dry deposition. This effect may be as much as 50 mg N m^{-2} yr^{-1} which is hardly more than 10% of total deposition in a near-source cell (Figure 2).

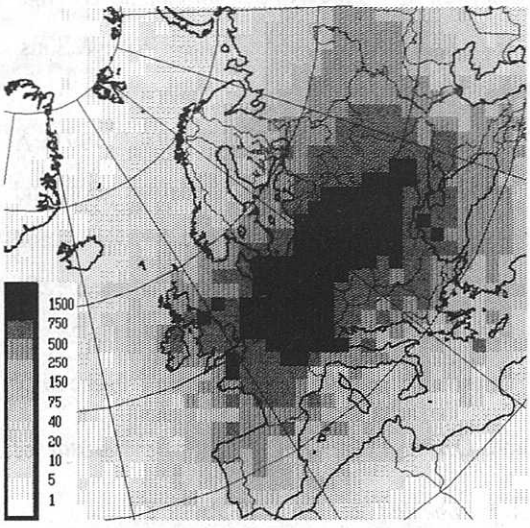

Figure 1 *Total NH_x deposition averaged over 1987-1994. Unit: mg N / m^2 yr*

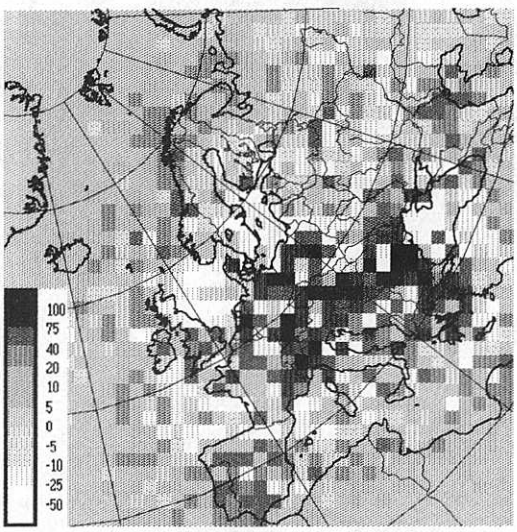

Figure 2 *Absolute difference in NH_x deposition for step 4 versus reference step. Unit=mg N / m^2 yr.*

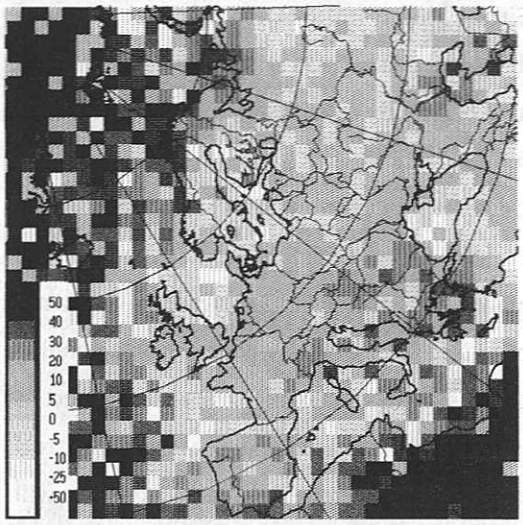

Figure 3 *Relative difference in ammonium deposition for step 4 versus reference step. Unit=%.*

At the same time there is a considerable increase of the total transport length of ammonia while the acidic emission reduces. This effect is well seen from Figure 3 which shows the increase of ammonium deposition in remote regions. Absolute values are quite small (~ 10 mg of NH_3 m^{-2} yr^{-1}) but their relative values are big (about 50-100%).

This effect is considerable in almost all far-located regions without own ammonium emission: Arctic, Scandinavia, Atlantic, Mediterranean and Africa. To explain this trend it is necessary to take into account that washout coefficient of ammonia is less than one of ammonium (the first one is a gas while the second one is aerosol). Bearing in mind increase of wet deposition while the distance from source increases, the following sequence could be created: decrease of acidic emission → increase of ammonia concentrations → decrease of wet deposition intensity → increase of the length of transport.

Finally it is worth mention that both of above described deposition variations are rather small and hardly be significant today and in near future.

Considering concentration variations it should be stated that deviation is much higher and ammonia concentrations increase by the factor of times together with corresponding decreasing of ammonium ones. This effect is rather an 'artificial' one than the real redistribution. Probably other oxidants will transform ammonia to ammonium anyway but this is the problem for future investigations.

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SHORT RANGE EXCHANGES OF ATMOSPHERIC AMMONIA, EMITTED FROM SLURRY, WITH GRASSLAND.

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Abstract - Novel applications of micrometeorological mass balance and wind tunnel techniques were used to investigate short range ammonia exchanges from slurry applications. Small plot experiments, using wind tunnels, and field scale micrometeorological experiments were conducted in the spring and summer respectively, on grassland for silage production.

Spring measurements showed rapid deposition of ammonia with fluxes ranging to -114 $\mu g\ m^{-2}\ s^{-1}$. A linear relationship was found between flux and mean air concentration, showing that no sink saturation occurred, and a sward compensation point of 74 $\mu g\ m^{-3}$ was estimated. Micrometeorological field experiments also showed rapid ammonia deposition with fluxes ranging to -10 $\mu g\ m^{-2}\ s^{-1}$. Deposition velocities decreased exponentially with time suggesting rapid saturation of the leaf surface sink, and that a variable compensation point occurred. In total, 62% of the ammonia emitted was deposited to the adjacent grassland within 50 m.

1. INTRODUCTION

Concentrations of ammonia (NH_3) in the atmosphere over Europe have doubled since 1950 (ApSimon *et al.*, 1987), resulting in increased atmospheric inputs to natural and semi-natural ecosystems. Enhanced ammonia deposition to heathlands (van der Eerden *et al.*, 1990) and grasslands (Fangmeier *et al.*, 1994) may reduce species diversity, and deposition to forests on poorly buffered soils can increase soil acidification through the microbial oxidation of ammonia to nitric acid (Draaijers *et al.*, 1989).

Recent estimates suggest that emissions from agricultural sources account for 90% of the total annual UK atmospheric inputs of ammonia (Sutton *et al.*, 1995). It is important, however, to identify the fraction of the ammonia that is transported regionally, as a significant fraction may be deposited on a local scale.

In this paper, adaptions of two methods for field investigations of ammonia exchange, the wind tunnel method for comparative studies and the mass balance micrometeorological method, were used in the measurement of such exchanges with grassland.

2. METHODS

2.1 Wind tunnel

Small plot wind tunnel experiments were conducted during the spring on a grass-clover field at North Wyke Research Station in Devon. The soil was an acidic sandy-loam and sward height was approximated to 0.2 m.

A system of four small wind tunnels was used based on that described by Lockyer (1984). In our experiments each tunnel system comprising two 2.0 m long x 0.5 m high x 0.5 m wide polycarbonate canopies coupled in series. A fan housed in a circular cross section steel duct drew air through both canopies at 1 m s^{-1} and air volumes passing through each canopy (v) were calculated.

Cattle slurry was applied beneath the first canopy, furthest from the turbine (canopy A) and the second (canopy B) covered an area of untreated grass sward.

Atmospheric ammonia concentrations (χ) were measured by drawing air through absorption flasks, containing 0.01 M ortho-phosphoric acid, at 66.7 ml s^{-1}. Measurements were made, from a single sampling point, at the inlet of canopy A (χ_i) and, from multiple sampling points across the canopy cross section, at the junction between canopies A and B(χ_j) and at the outlet of the turbine housing (χ_o).

Mean ammonia air concentrations in the exchange canopies ($\bar{\chi}$)were calculated from the average of χ_o and χ_j.

$$\bar{\chi} = \frac{\chi_j + \chi_o}{2} \qquad (1)$$

Emission and exchange fluxes were calculated from the difference between the mass of ammonia entering and exiting each canopy, of ground area A, over each experimental period (t). Emission (F_E) and exchange (F_x) fluxes are:

$$F_E = \frac{v(\chi_j - \chi_i)}{t\ A} \qquad (2)$$

$$F_X = \frac{v(\chi_o - \chi_j)}{t\ A} \qquad (3)$$

Attention was paid to ensuring air leaks could not occur along air lines or between canopies and before experimentation canopies were dried to prevent ammonia depositing to condensation. Pumps, gas meters, and logging equipment were housed in a box trailer.

Ammonia emissions from the slurry were varied by changing the area under canopy A over which slurry was spread. This was done by moving the slurry front to 0.25, 0.50 and 0.75 m from the canopy junction.

2.2 Micrometeorological mass balance

Field scale experiments were made on a 7.4 ha flat *Lolium perenne* L. field, with an acidic clay loam soil type, during the summer. Two rectangles (50 x 144 m) of untreated uncut grassland (sward height= 0.3 m) were separated by

Run	Mean Emission Flux ($\mu g\ m^{-2} s^{-1}$)			Mean Exchange Flux ($\mu g\ m^{-2} s^{-1}$)		
	0-3 hours	3-6 hours	6-9 hours	0-3 hours	3-6 hours	6-9 hours
	110	38	16	-31	-12	-4
	58	38	15	-25	-13	-4
	39	27	13	-11	-7	-5
	175	90	32	-82	-35	-13
	185	104	40	-114	-47	-17
6	141	87	38	-33	-25	-6

Table 1: Results of the wind tunnel experiments. Negative fluxes denotes deposition.

a cut strip (26 x 114 m) on which 7.5 tonnes of slurry was surface spread. A slurry injector with the tines raised was used to ensure a uniform slurry application and a constant fetch (x).

Wind direction at 3 m and wind speed at 1.6 m above the soil surface were measured, as were soil temperature and air temperature. Passive flux samplers, as described by Leuning *et al* (1984), were used in the measurement of mean horizontal ammonia fluxes ($\overline{u\ \chi}$).

Emission and exchange fluxes were calculated using the mass balance method as described by Wilson *et al* (1982). Horizontal fluxes were measured to 3 m above the soil surface at the upwind ($\overline{u\ \rho_h}$) and downwind ($\overline{u\ \rho_g}$) edges of the slurry strip, using 3 and 6 sampler heights (z) respectively, and to 6 m above the soil surface 46 m west of the slurry strip, using 10 sampler heights ($\overline{u\ \rho_d}$). Fetches across the strip (x_1) and adjacent grassland (x_2) were calculated from wind direction data and plot dimensions. Emission flux (F_E) and exchange flux (F_x) are:

$$F_E = \frac{1}{x_1} \int_{z_0}^{z_p} (\overline{u\ \chi_g} - \overline{u\ \chi_h})\ dz \quad (4)$$

$$F_X = \frac{1}{x_2} \int_{z_0}^{z_p} (\overline{u\ \chi_d} - \overline{u\ \chi_g})\ dz \quad (5)$$

At 1.6 m above the soil surface the mean ammonia air concentration across the untreated grassland plot (χ) was estimated by taking average of the air concentration at the slurry edge and that at 46 m west.

3. RESULTS

3.1 Wind tunnel experiments

Rapid deposition of ammonia occurred in all experiments immediately following slurry spreading (Table 1) with mean initial exchange fluxes ranging between -11 and -114 $\mu g\ m^{-2} s^{-1}$. Emissions and exchanges reduced linearly over 9 hours in all experiments. Figure 1 illustrates the linear correlation between mean ammonia concentration in air in canopy B and exchange flux, indicating that no sink saturation occurred. From the regression line a sward compensation point was determined to be 74 $\mu g\ m^{-3}$.

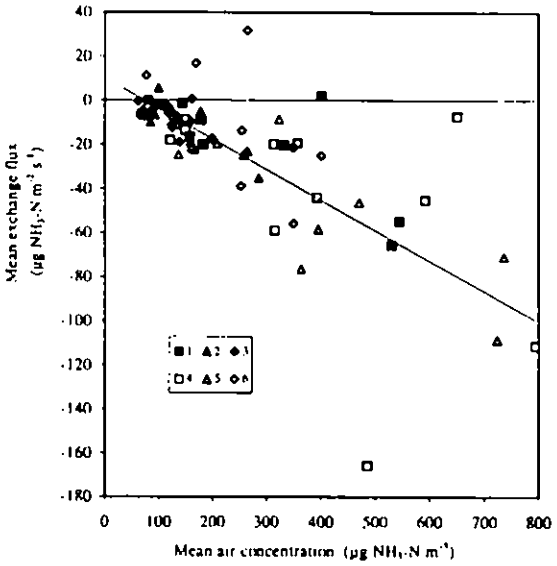

Figure 1: Relationship between air concentration and ammonia exchange as measured in the wind tunnels. Experiment numbers in legend

3.2 Micrometeorological experiments

Summary information on the emission and exchange results is shown in Table 2. Following surface spreading, ammonia rapidly volatilised from the slurry strip and then deposited to the adjacent grassland.

An emission flux of 26.07 $\mu g\ m^{-2} s^{-1}$ and exchange flux of -10.07 $\mu g\ m^{-2} s^{-1}$ was found, resulting in 65% of the total emission and 76% of the total deposition occurring during this first 5 hour run.

Exchange fluxes were lowest during Run 4 at -0.03 $\mu g\ m^{-2} s^{-1}$, despite continuous ammonia emission from the slurry strip. Emissions of ammonia from the slurry strip were lower during Run 5 than Run 4 but, over the adjacent grassland, deposition fluxes increased to -0.42 $\mu g\ m^{-2} s^{-1}$.

Run	Date/Time (GMT)	Mean Flux ($\mu g\ m^{-2} s^{-1}$)	
		Emission	Exchange
	5/7 11:58 - 5/7 16:46	26.07	-10.07
	5/7 16:55 - 5/7 12:28	3.02	-1.19
	5/7 21:43 - 6/7 10:56	2.02	-0.30
	6/7 11:00 - 6/7 16:23	1.63	-0.03
5	6/7 16:30 - 7/7 12:56	0.82	-0.42

Table 2: Results of the micrometeorological experiments. Negative fluxes denotes deposition.

A polynomial relationship was established between mean ammonia air concentration across the sward and exchange flux (Figure 3), illustrating the rapid saturation of the surface sink and showing that a variable compensation point occurred during Runs 3, 4, and 5.

Of the 6225 g of ammonium-N applied, 33% was emitted in total as NH_3 gas. Of that emitted, 62% was deposited and 38% was transported further than 50 m.

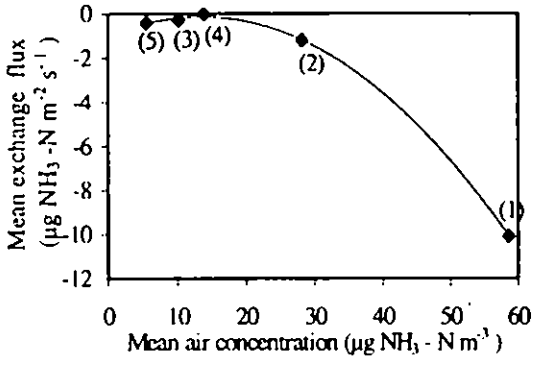

Figure 2: The relationship between air concentration and ammonia exchange measured by the micrometerological method. Run numbers in parenthesis

4. DISCUSSION

Spring measurements using the wind tunnels showed no sink saturation as exchange fluxes decreased linearly as mean air concentrations declined. This compares with the results of Whitehead and Lockyer (1987) and Farquhar *et al.* (1980) who both found no evidence for sink saturation in plants exposed to high concentrations of ammonia. Contrasting results were found from the summer micrometerological experiment where sink saturation began to occur 5 hours after spreading. Sommer and Jensen (1991) found similar results showing sink saturation close to a strongly emitting building. This suggests that ammonia exchanges may show seasonal differences dependent on sink conditions.

A compensation point of 74 µg m^{-3} NH_3-N at 10-14 °C was determined from the spring studies, which is far greater than the stomatal compensation point (χ_{cp}) determined by Farquhar *et al.* (1980) of 1.7 µg m^{-3} at 26 °C and 3.7 µg m^{-3} at 33 °C. This suggests a sward compensation point existed and that deposition was predominantly to the leaf surfaces.

Fluxes were bidirectional about this compensation point, with both emission and deposition occurring dependant on the leaf surface - air concentration gradient.

A variable sward compensation point was determined from the summer studies. These results compare with those found by Sutton *et al.* (1993) over fertilised vegetation in which ammonia readily deposited to the leaf surfaces when they have a high capacitance (wetness). When surfaces are dry no sink exists and ammonia is emitted from the stomata to the atmosphere. This is clearly shown in this study by the low deposition fluxes during the dry midday (Run 4) which increased during the cool overnight (Run 5) when the canopy was wetted by dew formation despite reduced mean ammonia air concentrations.

5. CONCLUSIONS

Grass swards adjacent to a slurry treated plot have a high surface affinity for emitted ammonia depending on the surface capacitance. This may result in differences between seasons. During cool wet periods, surfaces may adsorb considerable quantities of ammonia, but a compensation point may occur, resulting in re-emission of deposited ammonia from the sward. Due to diurnal patterns of wetting and drying in warmer conditions, the capacitance of the surface sink for ammonia may vary. This may result in sink saturation and emission of ammonia from the stomata directly to the atmosphere.

ACKNOWLEDGEMENTS

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MEASUREMENTS OF EMISSION AND DEPOSITION OF AMMONIA DURING THE ASEPS PROJECT

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Abstract - Measurements of atmospheric NH_3 and NH_4 ($NH_3 + NH_4^+$) in the sea have been carried out within the frame of the Air Sea Exchange Process Study (ASEPS) project. The air measurements were carried out by using diffusion scrubbers and diffusion denuders in different heights at two different locations at the coast of the island Lolland in Denmark. Seawater samples were collected from different locations and different depths and later analysed. Emission from the sea will occur when the NH_4 concentration in the water is high relative to atmospheric concentration. The atmospheric NH_3 measurements showed emission profiles in periods in which the concentrations of seawater NH_4 were too low to explain them. Surface microlayer measurements of NH_4 showed higher concentrations than in the bulk water which at least in part can explain the emission.

1. INTRODUCTION

The ASEPS project is a joint field experiment with National Environmental Research Institute (Denmark), Risø National Laboratory (Denmark), University of Hamburg (Germany) and TNO (the Netherlands) as participants. The overall aim of the project is to understand and parameterize the processes that leads to exchange of properties between the air and the sea.

2. EXPERIMENTAL SETUP

The experiments were carried out in October-November 1994 and April-May 1995 at the coast of the island Lolland in Denmark. Atmospheric ammonia measurements took place in a mast on the shore (5 metres from the shore) and in an offshore mast 1 km from the shore. The mast has been raised in connection with the establishment of an offshore windmill park. At the land mast NH_3 measurements were carried out simultaneously in three different heights (4, 9 and 14 metres) by using the diffusion scrubber technique (see below) with 10 min. Sampling time and measurement every one hour. At the sea mast diffusion denuders (see below) were used for measurements in five different heights (5.1, 6.8, 9.1, 14 and 19.5 metres) simultaneously. The sampling time was 6 to 12 hours. Sea water samples were collected at different locations in the vicinity of the sea mast by using a motor boat. The analytical system is described below.

3. MEASURING METHODS

3.1 Measurements of atmospheric ammonia

The diffusion scrubber
The collection device (the diffusion scrubber) consists of a tube with a water saturated microporous membrane centred along the axis of an outer glass tube. When atmospheric air is drawn through the glass tube at laminar flow ammonia will diffuse to the membrane due to the high solubility of ammonia in water. Particulate ammonium will follow the laminar flow out of the diffusion scrubber without being collected due to its smaller diffusivity compared with ammonia. The collection time is 10 min. After sampling of ammonia in the water, the ammonia containing water is pumped into a flow injection system where it reacts at 85°C with o-phthaldialdehyde and sulfite to the fluorescense product 1-sulfonatoisoindole, which is detected by a fluorescens detector in site. Since the collection efficiency is less than 100%, it is necessary to calibrate the system in order to determine the atmospheric concentrations. This is done by using a permeation tube placed in a temperature controlled oven. The detection limit for the diffusion scrubber is estimated to be 0.02 $\mu g\ m^{-3}$ Sørensen *et al.* (1994). During the Vindeby measurements the best obtainable detection limit was 0.2 $\mu g\ m^{-3}$.

Diffusion denuders:
A diffusion denuder (DD) is a glass tube, which when measuring ammonia is coated with oxalic acid. The DD makes use of the different diffusivity between gases and particles to separate atmospheric ammonia from particulate ammonium. When atmospheric air is drawn through the DD ammonia diffuses to the internal tube wall. After sampling the tubes are sealed and afterwards brought to the laboratory for analysis. The detection limit is dependent on the sampling time.

Measurements of seawater ammonia/ammonium (NH_4)
Water samples from different depths were collected by using a special bucket that could be closed at the required depth. Water samples of the surface microlayer was collected using a sieve. After collection the sealed water samples was brought to a mobile laboratory and analysed within one hour from collection.

3.2 The analytical system

A sample is injected in a flow injection system and by adding sodium hydroxide/citrate reagent the alkalinity is raised in order to convert all the ammonium to ammonia. The ammonia diffuses through a hydrophobic teflon membrane where it is collected by a neutral waterstream. The ammonia containing water reacts with o-phthaldialdehyde and sulfite as described in the diffusion scrubber section. The detection limit is 15 nmol l^{-1}.

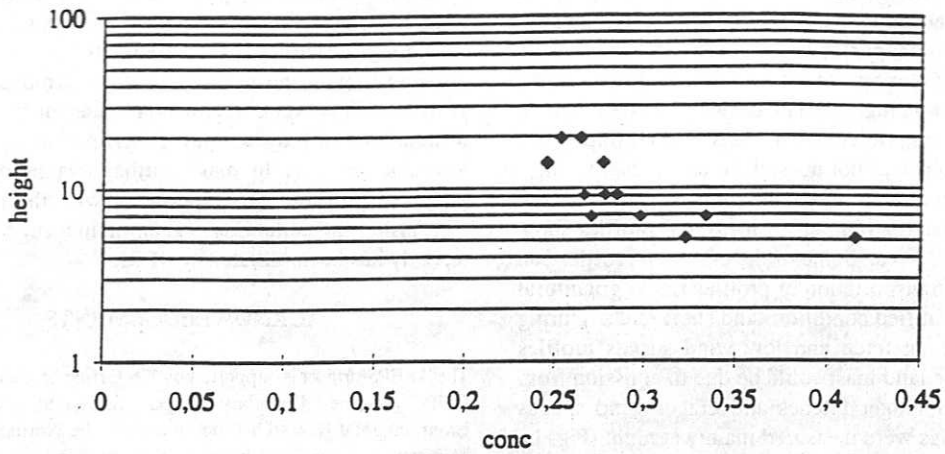

Figure 1: Emission profile measured during nightime. Concentration in $\mu g\ m^{-3}$.

4. MEASUREMENTS AND THEORY

There exist today only few direct measurements of ammonia equilibrium concentrations in the seawater/atmosphere system (e.g. Quinn *et al.* 1992). Data for the solubility of ammonia in fresh water based on measurements exist, however these data cannot be used directly as solubility data for ammonia in seawater. The reason for this is the fact that the salinity in the seawater changes the activity of both NH_4^+(aq) and NH_3*H_2O and thereby the overall solubility. An equation for the solubility of ammonia in seawater which takes salinity into account by combining different experimental works has been made by Asman *et al.* (1994). We have used this equation to calculate the equilibrium concentration of NH_3 in air (c_{eq}) from measurements of the NH_x concentrations in the water. The equilibrium air concentrations have been compared with the actual and ammonia concentrations

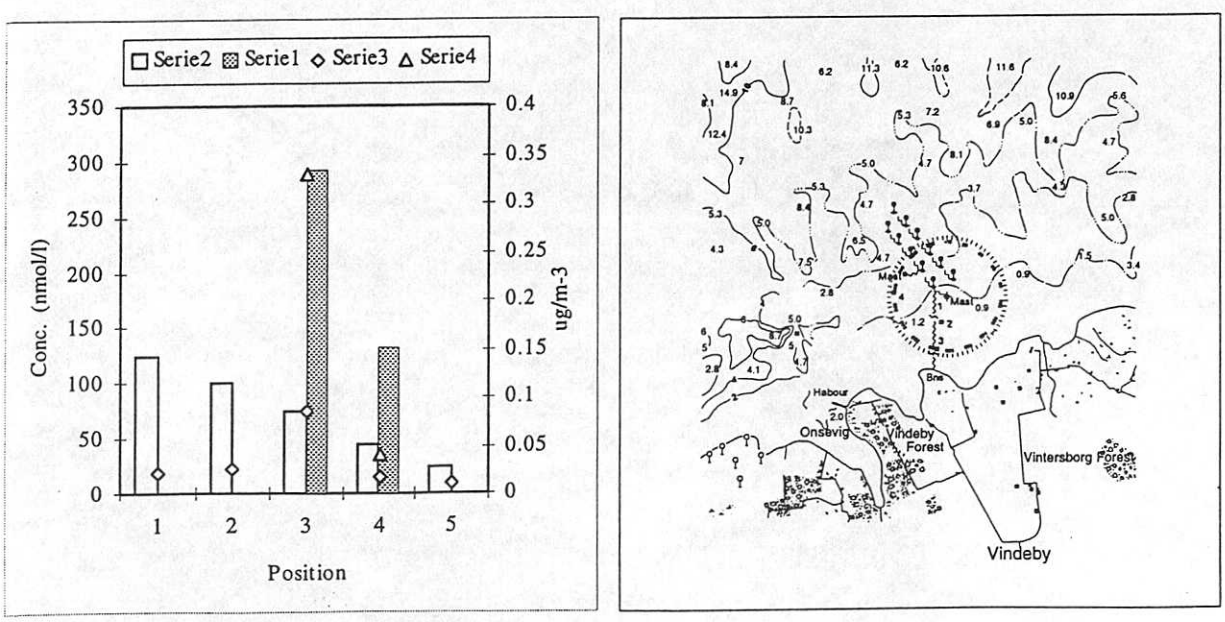

Figure 2. NH_x measurement of the bulk water and surface microlayer. The map shows the locations of the measurement positions.
Serie 1: surface microlayer NH_x measurements ($nmol^{-1}$)
Serie 2: bulk water NH_x measurements ($nmol^{-1}$)
Serie 3: calculated c_{eq} based on bulk water NH_x measurements ($\mu g\ m^{-3}$)
Serie 4: calculated c_{eq} based on surface microlayer NH_x measurements ($\mu g\ m^{-3}$)

measured by the diffusion scrubbers and the diffusion denuders.

Emission of NH_3 occurs when the temperature, pH and concentration of NH_4 in the water or in surface microlayer of the water, is high and the atmospheric background concentration of NH_3 is low. These events are hypothesized to happen at night where there is no algae production and during seasons where the decay rate of micro-organisms is high, i.e. late summer and fall. Due to very low atmospheric concentrations of NH_3 during the fall experiment it was not possible to detect any profiles. The NH_3 concentrations during the spring experiment were generally high and a big part of measured profiles show emission from the sea. Some of the emission profiles can originate from transportation of profiles from agricultural areas during stratified conditions and short fetch. During periods with long fetch and low wind speeds profiles measured at the land mast could be due to emission from the beach. At longer fetches and higher wind speeds emission profiles were measured mainly at night (Fig. 1).

The measured NH_4 concentrations in the sea displays a high horizontal variability (Fig. 2) and in general higher values in fall than in the spring. In general the calculated c_{eq} values for the spring experiment is much lower (a factor 10-100) than the measured atmospheric ammonia concentrations suggesting a constant deposition of ammonia to the sea. However measurements of the aqueous microlayer that is in direct contact with the atmosphere shows higher NH_4 concentrations than the bulk water (Fig. 2). This indicates that the equilibrium concentration, c_{eq} in the atmosphere just over the sea surface in reality might be higher than estimated from the bulk water samples. Unfortunately no microlayer measurements were performed during nighttime when the emission events occurred.

5. CONCLUSION

The pattern of emission events needs to be better quantified and parameterized. The NH_4 concentration in the microlayer must be measured more frequently in order to get more realistic time series of the temporal and spatial variability. Microlayer measurements have to be carried out jointly with the measurements of atmospheric NH_3 profiles. Moreover experimental values of the solubility of ammonia in seawater and experimental c_{eq} values, is desirable in order to make further evaluations on the observed profiles. An experiment with the purpose of measuring the solubility of ammonia in seawater is recently has been initiated at NERI.

ACKNOWLEDGEMENTS

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AMMONIA TRANSPORT IN A WELL-FERTILIZED PASTURE: DAILY FLUCTUATIONS

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ABSTRACT

Ammonia (NH_3) transport and the daily variability in NH_3 fluxes on a well-fertilized pasture were analyzed. The gradient-diffusion micrometeorological technique was used to determine NH_3 fluxes. The fertilized pasture showed a net uptake of aerial NH_3. Management practices which influenced NH_3 fluxes included fertilizer application and mowing (by grass wilting and windrowing). Variation in diurnal NH_3 flux was apparently caused by a higher diffusive resistance during nighttime than during daytime. Generally, the NH_3 compensation point was not different for day and night. This factor was dependent on plant N and soil water content.

Key words: Ammonia, transport, pasture, management, fertilizer.

INTRODUCTION

In NW Europe ruminant animal production is mainly based on herbage production (consumption) from fertilized pastures. However, this animal production system is a major source of ammonia (NH_3) losses (Jarvis and Pain, 1990). Measurements have been made on grasslands to determine NH_3 loss rates of N fertilizer (Velthof et al., 1990), livestock waste application (Pain et al., 1989) and the waste products of the grazing animal (Bussink, 1992) but the effect of the grass crop itself and of grassland management on NH_3 losses has not been specifically addressed. The purpose of this study was to analyze NH_3 transport and daily variability in NH_3 fluxes on a well-fertilized pasture.

EXPERIMENTAL

This study was conducted in a 10-ha perennial ryegrass pasture (*Lolium perenne*, L.) on calcareous clay soil at Swifterbant (52° 35'N, 5° 40'E). The pasture had been intensively managed in previous years and for this study was mowed for silage five times during the growing season. Nitrogen application was 480 kg ha^{-1} yr^{-1}. Measurements were made during the growing period of the 2nd (May/June) and 4th (August) cut. Nitrogen amendment for these two cuts received 100 and 80 kg N ha^{-1} as $Ca(NO_3)_2$, respectively.

Aerial [NH_3] measurements were made at seven heights (0 - 2m) for 17 periods of 24 hrs each, at 2 hr intervals by using gas-washing techniques (Bussink et al., 1996). The measurements usually started at noon. The gradient-diffusion micrometeorological technique (Denmead et al., 1976; Harper et al., 1987) was used to determine NH_3 fluxes. Soil and environmental conditions were measured including incident radiation, rainfall, soil temperature, and soil water content. For further discussion of the sampling and measuring techniques, see Bussink et al. (1996) and Harper et al. (1996).

RESULTS AND DISCUSSION

Cumulative NH_3 flux

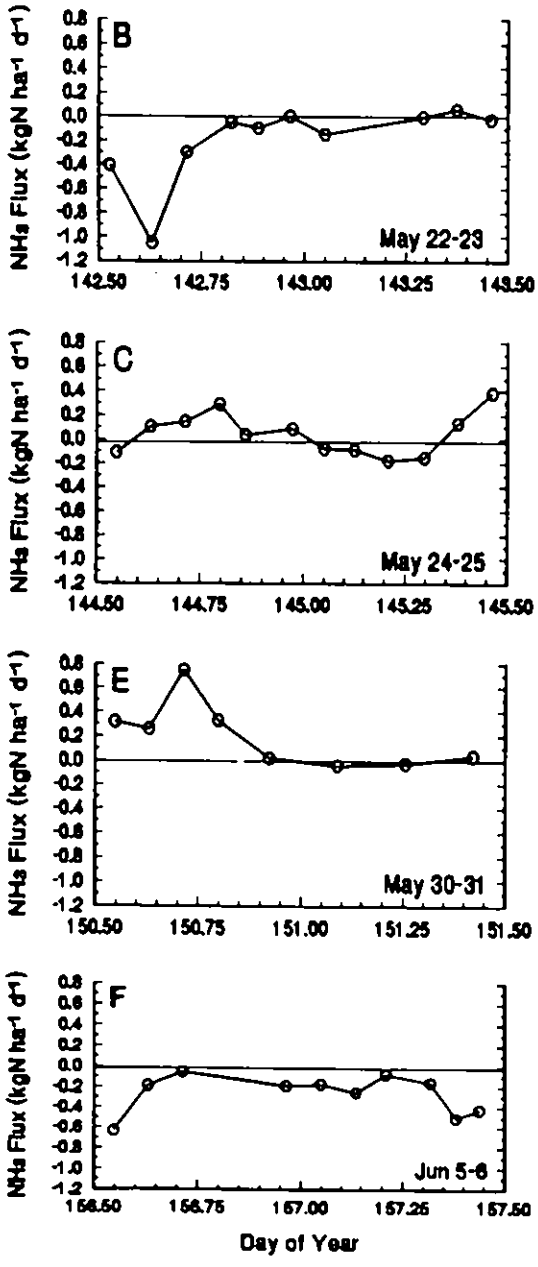
Absorbed atmospheric NH_3 amounted to be 2.3 ± 1.7 kg N ha^{-1} during the growing period of the second (spring) cut or about 12% of the harvested N *not* derived from fertilizer (about 3% of the total harvested N). Absorbed atmospheric NH_3 during the growing period of the fourth (summer) cut amounted to 3.9 ± 0.9 kg N ha^{-1} or about 11% of the grass N not derived from fertilizer (4% of the total harvested grass N). The amount of NH_3 absorbed in the fourth cut was larger than in the second cut since soil water content was more favorable during that growing period, allowing maximum stomatal opening and larger amounts of NH_3 absorption.

Diurnal Fluxes

Figure 1 presents NH_3 fluxes for selected periods showing daily changes in NH_3 transport (positive fluxes represent an efflux). A brief discussion of environmental and management effects on the diurnal fluxes are given with each figure (for further discussion of the two cutting seasons' NH_3 transport, see Bussink et al., 1996).

These graphs showed three interesting phenomena (i) NH_3 uptake immediately after mowing (1B, 1I), (ii) NH_3 efflux after $Ca(NO_3)_2$ application (1C, 1E, 1J and 1K) and (iii) NH_3 uptake (1F) when there

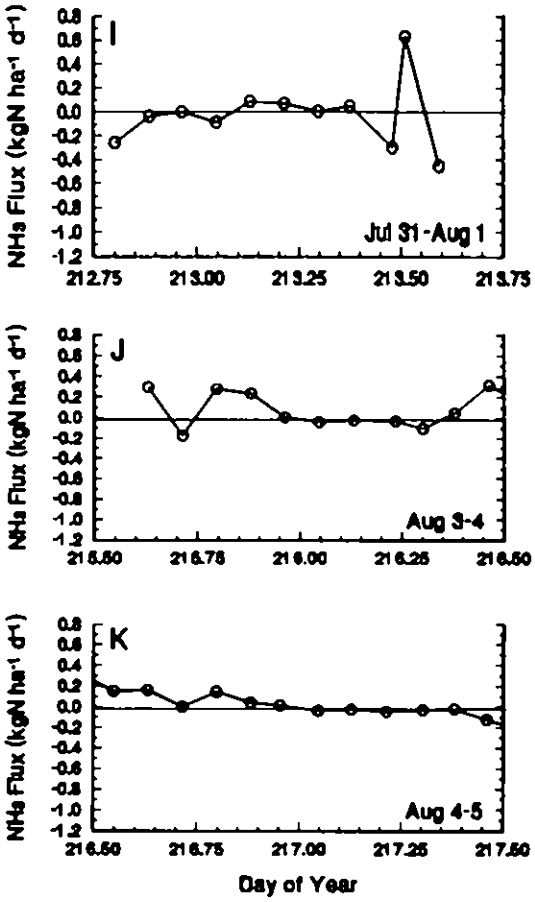
Figure 1. Some characteristic daily NH_3 fluxes during the growing periods of the second (spring) and fourth (summer) cut.



The pasture (first cut) was mown around noon on May 22. Immediately after mowing there was a net uptake of NH_3, possibly because photosynthesis of the mown grass continued for a while.

Fertilizer was applied in the morning of May 24. After two weeks without rainfall, a few mm of rainfall was observed on May 29, 30 and 31. All fertilizer was dissolved on May 29. The amount of available soil N was high (50 kg N ha^{-1} in the layer 0-5 cm), which resulted in a high N uptake rate by the grass. Excess NO_3^- uptake may have been released as NH_3.

More than 40 mm of rainfall was observed between May 31 and June 6 (of which about 10 mm on June 5). The amount of available soil N was reduced to a few kg in the 0-5 cm layer. From June 5 on all daily NH_3 fluxes of the remaining part of the growing period of the second cut were negative.



The pasture was mown around noon on July 31. The spike on August 1 could be a measurement error, however it coincided with tedding and windrowing. The sharp drop of the spike coincided with removing of the herbage. This spike could not be observed on May 23, because aerial measurements stopped before windrowing and removing the herbage.

Fertilizer was applied in the morning of August 2. The amount of available soil N increased to about 45 kg N ha^{-1} (in the layer 0-5 cm) on August 4, which resulted in a high N uptake rate by the grass. Excess NO_3^- on uptake on August 3 and 4 may have been released as NH_3. After August 5 all daily fluxes of the remaining part of the growing period of the fourth cut were negative.

was little mineral soil-N available. Kormos and Chestnutt (1967) have observed that dry matter yield production (photosynthesis) continued for some hours after mowing; however, the N supply by the roots is interrupted due to the cutting. Aerial NH_3 is absorbed in an effort to satisfy N demand for assimilation of amino acids from the organic acids (Harper et al., 1987) produced in photosynthesis before plant die-off.

The observed NH_3 efflux after N fertilizer application (1C, 1E, 1J and 1K) is in line with early studies (Eggleton, 1935; Webster, 1959) showing a buildup of NH_3 in grass after fertilizer application due to NO_3, with absorption being faster than it could be utilized. Harper et al. (1987) and Harper and Sharpe (1995) have shown NH_3 released under high soil minral N status during the vegetative growth period in wheat and corn. This efflux is observed during daytime because the reduction of excess NO_3 is an energy intensive process. High NH_4 may than be expected. For the same reason low soil N or plant N status may lead to uptake of NH_3, depending on plant species and NH_3 concentration in air.

Ammonia compensation point (NH_3CP)

The NH3CP is the ambient aerial [NH_3] at which the net NH_3 flux between plant and atmosphere is zero. If the aerial [NH_3] > NH_3CP then uptake of NH_3 will occur. If the aerial [NH_3] < NH_3CP then NH_3 will be released. Regression analysis showed a good correlation between aerial [NH_3], the NH_3 flux density (N_{NH3}, kg N ha^{-1} d^{-1}), grass N content (N_g, g kg^{-1} DM) and soil water content (SWC, cm^3 cm^{-3}) (Table 1). Inclusion of the 'factor period-of-day' improved the model ($p < 0.001$, $R^2 = 78\%$) compared to the model without this factor. Additionally the t probability of differences suggested that the

Table 1. Regression calculation results for the model log $(NH_3 \text{ in air})_{(d,n)} = a_{(d,n)} + b_{(d,n)} N_{NH3} + c_{(d,n)} N_g + e_{(d,n)} SWC$. The subscripts 'd' and 'n' are used for day and night, respectively. Model: $p < 0.001$, $R^2_{adjusted} = 78\%$.

Coefficient	Estimate				Standard error of differences	Probability of differences
	Day	Se	Night	Se		
$a_{d,n}$	0.544	0.306	0.195	0.347	0.462	0.457
$b_{d,n}$	-0.415	0.286	-1.911	0.924	0.967	0.108
$c_{d,n}$	0.0548	0.017	0.100	0.021	0.027	0.134
$e_{d,n}$	1.90	1.17	-1.32	1.21	1.687	0.067

relationship of log (aerial $[NH_3]$) with N_{NH3}, N_g and SWC was different for day and night conditions. The lower nighttime coefficient of N_{NH3} suggested a higher diffusive resistance ($p < 0.108$) at night for NH_3. This means that NH_3 is much more easily taken up or released by the crop during daytime than nighttime. For example, to get an NH_3 flux density rate of -0.1 kg N ha^{-1} d^{-1} under maximum growing conditions (N_g = 40 gN kg^{-1} and SWC = 0.4 cm^3 cm^{-3}), aerial daytime $[NH_3]$ would have to be 1.4 μg m^{-3} higher than the NH_3CP (39.1 μg m^{-3}). Likewise to get the same uptake rate at night, aerial $[NH_3]$ would have to be 8.2 μg m^{-3} higher than the NH_3CP (33.0 μg m^{-3}). Under bad growing conditions (N_g = 20 g N kg^{-1} and SWC = 0.25 cm^3 cm^{-3}), nighttime and daytime NH_3CP are much lower, being 6.5 and 8.3 μg m^{-3}, respectively. Paired testing for different N_g and SWC showed that differences between daytime and nighttime NH_3CP were generally not significant ($p < 0.05$). The effect of SWC was probably masked by soil temperature.

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MEASURING VERTICAL FLUX DENSITIES OF REACTIVE S- AND N-SPECIES USING (SLOW) DENUDER FILTER SAMPLERS AND A (FAST) MICROMETEOROLOGICAL METHOD (RATIOMETRIC METHOD)

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Abstract— The ratiometric method to determine vertical flux densities of matter from measurements of the vertical flux densities of heat and momentum (sonic anemometer) as well as two wind velocities, two air temperatures and two trace gas concentrations within the constant flux layer is described. The ratiometric method can be applied to sampling procedures with a low resolution in time (denuders, filters), if several pairs of samplers can be operated according to the prevailing atmospheric columnar conductance which is determined on-line. The applicability, availibility and robustness of this classifying sampling procedure was tested over about one vegetation period for the gases NH_3, HNO_2, HNO_3, SO_2 as well as NH_4^+, NO_3^- and SO_4^{2-} in aerosols above a barley field.

1. INTRODUCTION

The amount of matter exchanged between plant/soil systems and the atmosphere cannot be determined directly at the plant/atmosphere interface. This interface (envelope) is normally not defined nor physically detectable. From balance considerations one can deduce that in steady state net vertical fluxes of matter, energy and momentum within the atmosphere itself must be constant with height, if the atmosphere above the phytosphere is horizontally homogeneous and free of internal sources and sinks (concept of constant flux layer CFL). This means that vertical fluxes or flux densities within CFL have to be identical with those between atmosphere and phytosphere. Flux densities in CFL can be determined from vertical profiles of the respective concentrations of matter, wind velocities and air temperature applying the Monin-Obukhov similarity theory (Monin and Obukhov 1954, see also Etling 1987). The validity of this theory is restricted to dynamically induced turbulence which excludes cases with very low windspeeds (strongly stable stratification at night, and convection during the day).

The assumptions made to derive the CFL concept imply several restrictions on the treatment of vertical flux densities, in particular to steadiness and horizontal homogeneity. The assumption of steady conditions has proved to be reasonable for intervals of the scale of half an hour. However, horizontal homogeneity can be attributed to a comparatively narrow atmospheric layer, only. The lower boundary of this layer is at about twice the vegetation height, below this height individual roughness elements cause non-steady three-dimensional flow patterns (roughness sub-layer). The height of the upper boundary depends on the definition of "constant flux" which is normally thought to be constant within a variation of 10 %. A rough but reasonable estimate of the height of the upper boundary is 1 to 20 % of the fetch, i.e. the distance downwind from a change of surface features. However, the depth of CFL differs for different entities (Wyngaard 1985).

For the experimental determination of flux densities, the limited height range of CFL and the non-ideal resolution of the sensors restrict the number of technically reasonable measuring heights. Therefore, in most cases an adequate determination of the vertical profiles for concentrations, wind velocity and air temperature is difficult to achieve. In addition to that, due to the lack of a consistent theory for conditions of convection or strongly stable stratification, even adequately determined vertical profiles often cannot be processed to yield the respective vertical flux densities. These problems can be overcome to some extent by direct determination of fluxes via eddy correlation. While this is state of the art for heat, momentum and some trace gases, fast sensors are not available for most chemical species. Thus a technique was developed which combines the adequate (fast) sensoring of physical entities with the (slow) determination of concentration gradients by a method, which requires two measuring heights only.

2. RATIOMETRIC APPROACH FOR THE DETERMINATION OF VERTICAL FLUX DENSITIES OF GASES

In analogy to electric currents, the columnar flux densities F_E of conservative entities E between atmosphere and the plant/soil system may be decribed by

using models comprising potential differences ΔP_E as driving forces and columnar conductances λ_E or columnar resistances R_E characterizing the respective properties of the air column between two heights z_1 and z_2 within CFL:

$$F_E = -(\Delta P_E \cdot \lambda_E)$$
$$\text{or} \quad F_E = -\left(\Delta P_E \cdot \frac{1}{R_E}\right) \tag{1}$$

If one measures P_1 and P_2 at heights z_1 and z_2, respectively, upward fluxes are positive whenever ΔP_E is negative.

Within the constant flux layer, conductances and resistances can be derived from measurements of the profiles of horizontal wind velocity and air temperature. Due to the restrictions mentioned above, we favour the determination of the conductance of the air column by measuring flux density and driving force using a tracer which passes the same air column as the entitiy under consideration, thus making use of a system whose analogous circuit diagram is shown in Figure 1.

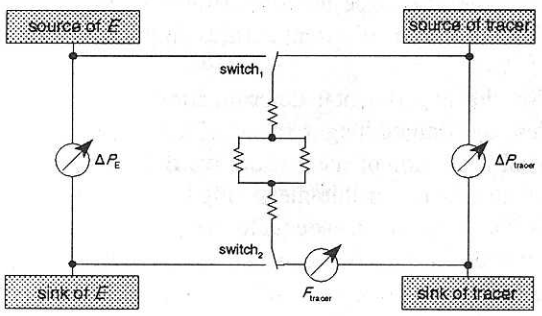

Fig. 1. Circuit diagram illustrating the determination of the total columnar resistance between z_1 and z_2 using bridge "wiring". The switches are operated at the same time and very fast. If momentum and sensible heat are used as tracers the simultaneous determination of the three entities needed to satisfy eqs. (9) and (10) can be achieved simultaneously.

Conductance for the tracer of the column can be determined as a whole, even if the column is stratified or horizontally heterogeneous:

$$\lambda_{tracer} = -\frac{F_{tracer}}{\Delta P_{tracer}} \tag{2}$$

If columnar conductivities of turbulent air can be attributed to the same transport mechanism, then

$$\frac{F_E}{F_{tracer}} = \frac{\Delta P_E}{\Delta P_{tracer}} \cdot \frac{\lambda_E}{\lambda_{tracer}} \tag{3}$$

This relation can be used for flux density measurements if

$$\frac{\lambda_E}{\lambda_{tracer}} = const. \tag{4}$$

It is convenient to use momentum and sensible heat as tracers.

The columnar conductivites are functions of the exchange coefficients k characteristic for the column and the entity exchanged:

$$F_m = -k_m \cdot \frac{\partial u}{\partial z} \tag{5}$$

$$F_h = -k_h \cdot \frac{\partial \theta}{\partial z} \tag{6}$$

$$F_A = -k_c \cdot \frac{\partial c_A}{\partial z} \tag{7}$$

k_m	exchange coefficient of momentum
k_h	exchange coefficient of sensible heat
k_c	exchange coefficient of gaseous matter
u	horizontal wind velocity
θ	air temperature
c	concentration of (gaseous) matter

It is generally assumed that for non-neutral stratification $k_c = k_h$, whereas $k_c = k_m$ for neutral stratification (proved to be correct within the limits of instrumentation for water vapour by Dyer and Hicks 1970 and Tanner 1960, for ozone by Droppo and Doran 1983). These turbulent exchange coefficients are linked by the following equation using empirical stability functions Φ_m and Φ_h the ratio of which becomes 1 in neutral stratification (cf Etling 1987):

$$k_{c_A} = k_{c_{O_3}} = k_{c_{H_2O}} = k_h = k_m \frac{\Phi_m}{\Phi_h} \tag{8}$$

Under the circumstances mentioned above the ratio of conductivites in eqs. 3 and 4 becomes 1. Thus the experimental determination of the flux densities of momentum, F_m, and sensible heat, F_h, together with 2 wind velocities u, 2 air temperatures θ and 2 concentrations c_A (mixing ratios χ_A, partial densities ρ_A) at an upper and a lower measuring height within the constant flux layer can be used to determine the flux of a trace gas A, F_A:

$$\Delta\theta = 0: \quad \frac{F_m}{\Delta u} = \frac{F_A}{\Delta \rho_A} \tag{9}$$

$$\Delta\theta \neq 0: \quad \frac{F_h}{\Delta\theta} = \frac{F_A}{\Delta \rho_A} \tag{10}$$

Assuming the validity of eq. 8, the same relation can be obtained by combination of eqs. 5 to 7 if the three functions are steady and strictly monotonous. As, by definition, the flux densities of matter, sensible heat and momentum are (approximately) independent of height, the fractions of the differentials $\partial c/\partial\theta$ or $\partial c/\partial u$ are independent of height as well and can be replaced by the respective fractions of differences (Huebert and Robert 1985, Meyers *et al.* 1989, Grünhage *et al.* 1994).

Because of its relation to the Bowen ratio method we call this method the **ratiometric method**.

$$F_{c_A} = \frac{F_h}{\Delta\theta} \quad \Delta\rho_A = - \lambda_h \cdot \Delta\rho_A$$
$$\text{or } F_{c_A} = \frac{F_m}{\Delta u} \quad \Delta\rho_A = - \lambda_m \quad \Delta\rho_A \qquad (11)$$

All entities required have to be measured simultaneously. Flux densities of momentum and sensible heat can be measured on-line using sonic anemometers within the same air column as the respective gases. Basic instrumentation complies

- concentration measurements at heights z_1 and z_2 (2 concentration monitors)
- air temperature measurements at heights z_1 and z_2 (2 ventilated resistance thermometers)
- horizontal wind velocity measurements at heights z_1 and z_2 (2 cup anemometers)
- direct measurement of the flux of sensible heat and direct measurement of the flux of momentum (1 sonic anemometer)
- PC for the on-line calculation of F_h and F_m, data logging and storage

The applicability of this ratiometric method is restricted to concentration measurements with a resolution in time of at least 30 minutes. It had already applied by Huebert & Robert (1985) and Meyers *et al.* (1989) for the determination of deposition of nitric acid. In contrast to our work they used denuders or filter packs with a resolution in time of one to three hours, assuming homogeneity and stationarity for their sampling periods.

However, such techniques cannot be applied to time-integrating measurements of the vertical flux densities of many reactive N- and S-species.

3. CLASSIFYING SAMPLING WITH DENUDERS AND FILTERS

Denuder filter techniques are often used to simultaneously determine concentrations and concentration gradients of gaseous and particulate N- and S-species. Their resolution in time normally is hours rather than minutes. Sampling times exceeding the scale of minutes lead to the violation of Reynold's averaging rules, if both λ and $\Delta\rho_A$ vary with time (see Figures 2 and 3):

$$\overline{\lambda \cdot \Delta\rho_A} \neq \overline{\lambda} \cdot \overline{\Delta\rho_A} \qquad (12)$$

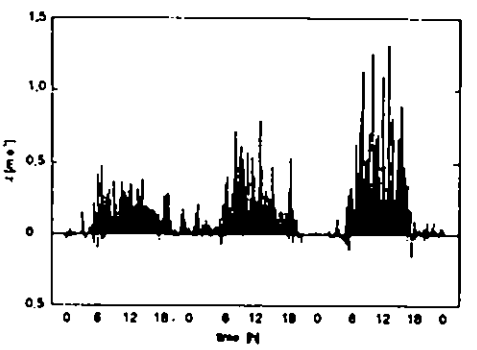

Fig. 2. Variation of λ during three summer days

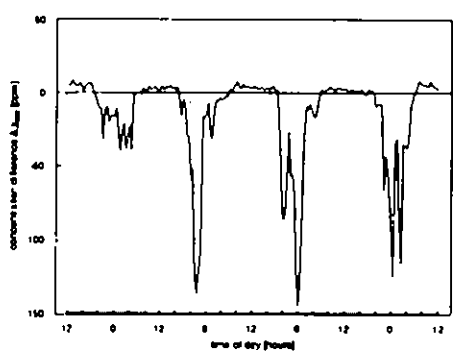

Fig. 3. Variation of the difference of partial densities $\Delta\chi$ for CO_2 above grassland during four summer days

For samplers with a low resolution in time, this problem can be overcome by classifying sampling: classes of λ are formed, and a pair of denuder filter samplers is then assigned to each class of λ. Classification of concentration differences can be achieved by permanent determination of λ and assuming that the conductivity of the air column in the next minute is in the same class as in the previous minute. Subsequently the means of ρ_A and λ are determined.

$$F_A = \frac{1}{T} \cdot \sum_{i=1}^{j} \overline{\lambda_i} \quad \overline{\Delta\rho_{A_i}} \cdot t_i \qquad (13)$$

$$\text{with} \qquad T = \sum_{i=1}^{j} t_i \qquad (14)$$

In our experiment we used j = 6 pairs of samplers for 6 classes of λ which, after screening measurements, we designed to be populated equally. Table 1 illustrates the results of this procedure for important meteorological parameters.

Table 1: Dependency of selected meteorological and micrometeorological parameters on λ interval; measuring period one week in July; percentage of λ_h: 76.2 %; percentage of λ_m: 23.8 % (Zimmerling 1994)

λ interval	I	II	III	IV	V	VI
from [m s^{-1}]	0	0.008	0.025	0.060	0.110	0.190
to [m s^{-1}]	0.008	0.025	0.060	0.110	0.190	5.0
F_m [m^2 s^{-2}]	- 0.0068	- 0.0198	- 0.0437	- 0.0670	- 0.0992	- 0.0774
F_h [K m s^{-1}]	- 0.0027	- 0.0045	+ 0.0205	+ 0.0670	+ 0.0992	+ 0.1391
λ [m s^{-1}]	0.0117	0.0319	0.0702	0.1141	0.1448	- 0.1871
θ [°C]	15.0	16.3	17.8	19.7	20.8	21.3
$\Delta\theta$ [K]	+ 1.04	+ 0.64	+ 0.04	- 0.42	- 0.60	- 0.72
u [m s^{-1}]	1.0	1.4	2.0	2.3	2.6	2.4
Δu [m s^{-1}]	+ 0.31	+ 0.50	+ 0.63	+ 0.68	+ 0.72	+ 0.63

4. TESTING THE CONCEPT USING FLUX DENSITIES OF HEAT AND MOMENTUM

In order to validate the assumptions mentioned above we "sampled" temperature and momentum analogously to concentration, calculated the respective cumulative flux densities and compared the results obtained from eddy correlation with those of classifying sampling.

Cumulative flux density of momentum:

eddy correlation:

$$\sum_{t=0}^{T} F_m = \sum_{t=0}^{T} u' \cdot w' \qquad (15)$$

ratiometric:

$$\sum_{t=0}^{T} F_m = \sum_{i=1}^{6} (\overline{\lambda_m})_i \cdot (\overline{\Delta u})_i \cdot t_i \qquad (16)$$

Cumulative flux density of sensible heat:

eddy correlation:

$$\sum_{t=0}^{T} F_h = \sum_{t=0}^{T} w' \cdot \theta' \qquad (17)$$

ratiometric:

$$\sum_{t=0}^{T} F_h = - \sum_{i=1}^{6} (\overline{\lambda_h})_i \cdot (\overline{\Delta\theta})_i \cdot t_i \qquad (18)$$

As can be deduced from Table 2, high percentages in λ_h resulted in good agreement for the two F_h, high percentages in λ_m in good agreement for F_m. Fluxes obtained from the classifying ratiometric method fall short of eddy fluxes. A mean bias of less then 10 % is in the same order of magnitude as the variation of "constant" flux. The influence of the quality of the concentration gradients exceeds this error by far. These considerations are supported by model calculations for ozone flux densities using classifying passive sampling techniques and the ratiometric method (Dämmgen *et al.* 1996).

5. EXEMPLARY RESULTS OF FLUX DENSITY MEASUREMENTS

Goal of this experiment was the evaluation of the applicability, availibility and robustness of method and equipment for the simultaneous determination of flux densities of NH_3, HNO_2, HNO_3 and SO_2 and of NH_4^+, NO_3^- and SO_4^{2-} in aerosols above a barley field. Concentration measurements were carried out using the KAPS denuder filter system (cyclone, three-stage annular denuder, dual filter pack, critical orifice; Peake and Legge 1987). The typical flow rate of the sampling system was 6.5 l min^{-1} leading to sampling volumes of at least 5 m^{-3} per measuring period. Measuring heights z_1 and z_2 were 3,5 m and 1 m above canopy. The average margins of analytical errors σ (in μg m^{-3}) were: SO_2: 0.4; HNO_3: 0.2; HNO_2: 0.1; NH_3: 0.2; SO_4-S: 0.1; NO_3-N: 0.1; NH_4-N: 0.1. F_h and F_m were determined from 10 min sliding means (Zimmerling 1994).

We made use of an experimental field readily equipped with the instrumentation for agrometeorology and a lysimeter basement we used for data logging and processing. Due to experimental restrictions fetch was insufficient in principle. Surface properties and water status of the adjacent fields were similar to those of the field under consideration thus yielding acceptable conditions for this experiment for most of the time. A period of slurry application in the neighbourhood clearly led to a violation of the basic assumptions for CFL. Results are given in Table 3; variations were calculated using normal error propagation comprising analytical data only.

Table 2. Comparison of the cumulative fluxes of sensible heat and momentum obtained from eddy correlation and from classifying ratiometric sampling; measuring station Braunschweig-Völkenrode (Zimmerling 1994)

week	percentages of λ_m and λ_b	cumulative fluxes of sensible heat [J m^{-2}]		cumulative fluxes of momentum [m^2 s^{-1}]	
		eddy correlation	ratiometric (% of eddy)	eddy correlation	ratiometric (% of eddy)
1	λ_m: 83.3 %; λ_b: 16.7 %	+ 4421	+ 3484 (79 %)	- 28795	- 27769 (97 %)
2	λ_m: 48.2 %; λ_b: 51.8 %	+ 13985	+ 11819 (85 %)	- 14471	- 13528 (94 %)
3	λ_m: 23.8 %; λ_b: 76.2 %	+ 36273	+ 35751 (99 %)	- 4929	- 4483 (91 %)

Table 3: Cumulative fluxes of reactive N- and S-species above a winter barley field (one vegetation period) (Zimmerling 1994)

	SO_2-S	SO_4-S	HNO_3-N	NO_3-N	HNO_2-N	NH_3-N	NH_4-N
kg ha^{-1}	- 4.5 (± 0.5)	- 1.6 (± 0.2)	- 1.0 (± 0.1)	0.1 (± 0.1)	0.1 (± 0.05)	+ 5.2 (± 0.3)	- 1.6 (± 0.3)

6. DISCUSSION

Adapted flow rates and accumulation times of denuder filter samplers result in adequate analytical precision: for most cases the concentration differences $\Delta\rho$ exceed 2σ. In practice, Reynold's averaging rules are not violated. Due to the averaging time of 10 min homogeneity and stationarity are achieved more often than for half hourly intervals. However, periods with insufficient fetch or stationarity cannot be identified after sampling. The set-up provides instrument for the continuous determination of flux densities over a long period with a resolution in time of days. As the sampling system is simple, trained personnel will have few difficulties to gain comparatively complete data sets. However, the procedure is labour intensive. A detailed presentation will be given in Zimmerling *et al.* (1997).

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AMMONIA CONCENTRATION AND DRY DEPOSITION OVER GRASSLAND IN GERMANY

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Abstract–Ammonia measurements with a continuous flow denuder system were carried out at three levels (0.76 m, 1.80 m, 4.53 m) above an extensive area of short grassland near Melpitz, Germany. The continuous measurements were made for 4 months and provided a data capture of >70%. Together with micrometeorological measurements, the results were used to quantify NH_3 exchange with the grassland.

The measurements showed both NH_3 deposition and emission fluxes. Ammonia "compensation points", estimated as the air concentrations at which there was a change in flux direction, existed mostly in the concentration range 0.5–2.0 μg m^{-3} (temperature range 0–28 °C), and little relationship with temperature was observed. For an example of three days, typical fluxes and deposition velocities are calculated. For measurements showing deposition, typical canopy resistances (R_c) are in the range 50–300 s m^{-1}. During periods with emission, the simple 'big leaf model' calculating R_c is not appropriate, and estimates of the NH_3 surface concentration are necessary.

Key word index: dry deposition, emission, ammonia, grassland

1. INTRODUCTION

Dry deposition is one of the final results of a chain of complex processes involving emission, dispersion and chemical transformation within the atmosphere. Dry deposition removal from the troposphere depends on the meteorological transfer properties of the atmospheric surface layer, the capability of the vegetation and soil to take up matter and the prevailing chemical and photochemical environment. The environmental conditions vary with the direction where the pollutants come from, the emission rates and the interrelation between air temperature and energy consumption /1, 2/. Ammonia (NH_3), as the most abundant alkaline component of the atmosphere, is an important trace gas because of its potential for acidification and because it may be important as a nitrogen source for ecosystems. NH_3 is also both deposited to and emitted from ecosystems, with changes in the flux direction being frequent /3/.

The first results of NH_3 concentration measurements and dry deposition calculations are presented from a study carried out over a large old meadow. The site lies in an agricultural region downwind of the conurbation of Leipzig on the research station of the IfT at Melpitz. There are also available micro-meteorological parameters from the national research project SANA (scientific observations program for the rehabilitation of the atmosphere above the new countries of Germany). The set-up of the station is described in /4/. The NH_3-gradient measurements were carried out with continuous flow denuder technique /5/ as one part of the EU-project "Towards Development of a deposition monitoring network for air pollution of Europe" (included in "LIFE").

2. EXPERIMENTAL AND CALCULATION

At the Melpitz research station, situated in the center of an old large flat meadow, the NH_3 gradient measurements were carried out with an "Amanda" gradient system, produced from ECN in the Netherlands. This is a continuous flow denuder system with three measuring levels. The levels in the study here are 0.76 m, 1.80 m, and 4.53 m above ground. Ammonia is captured into acid solutions in

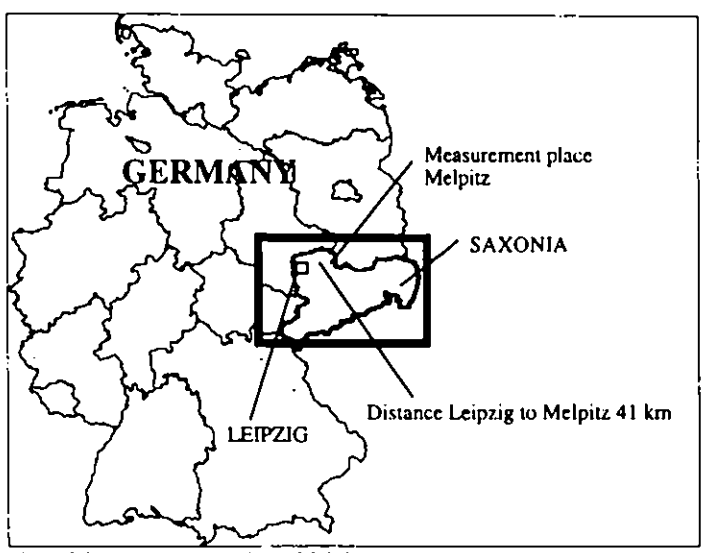

Fig. 1: Location of the measurement site at Melpitz.

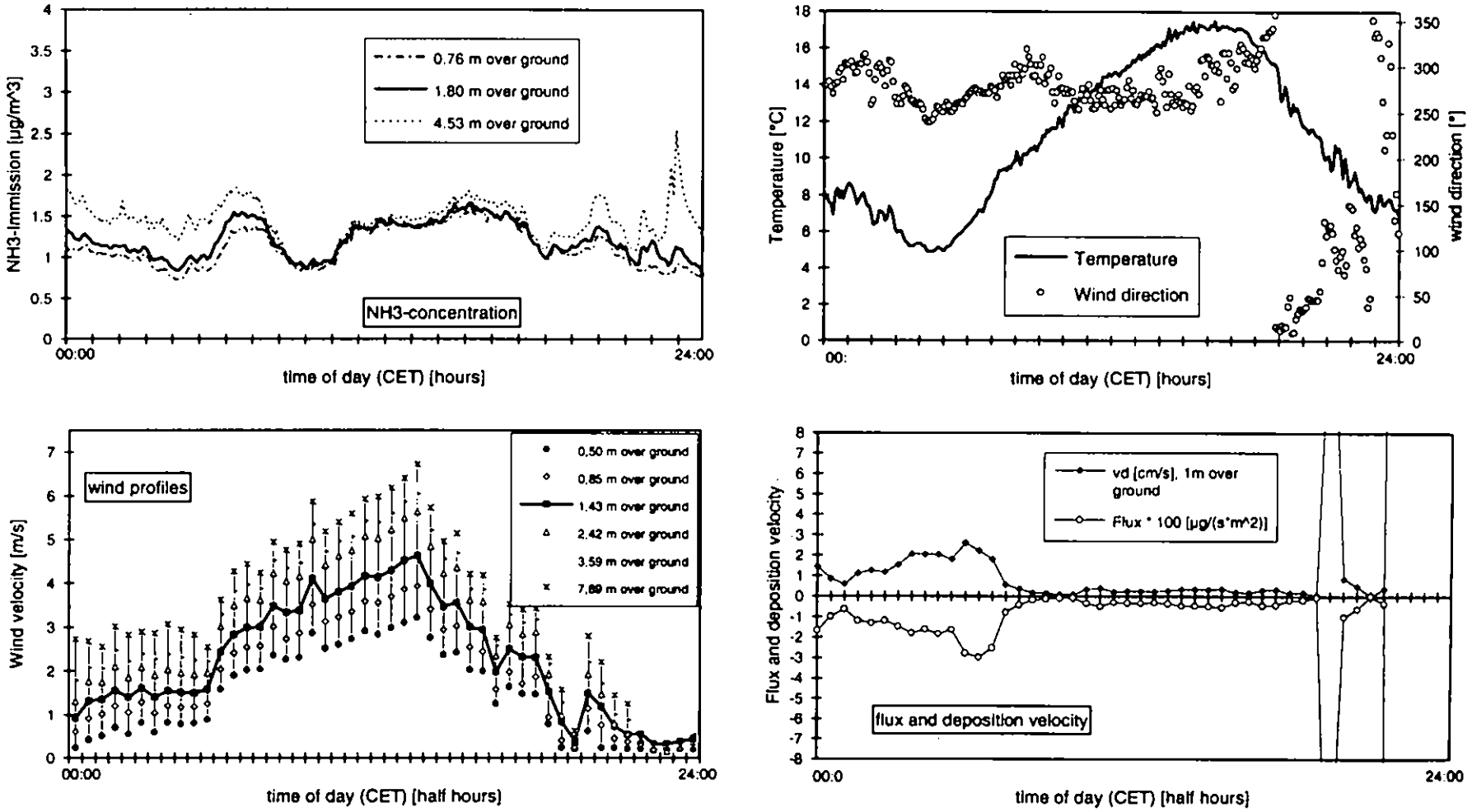

Fig. 2: Example of the gradient measurements for one example day (7/5/1995).

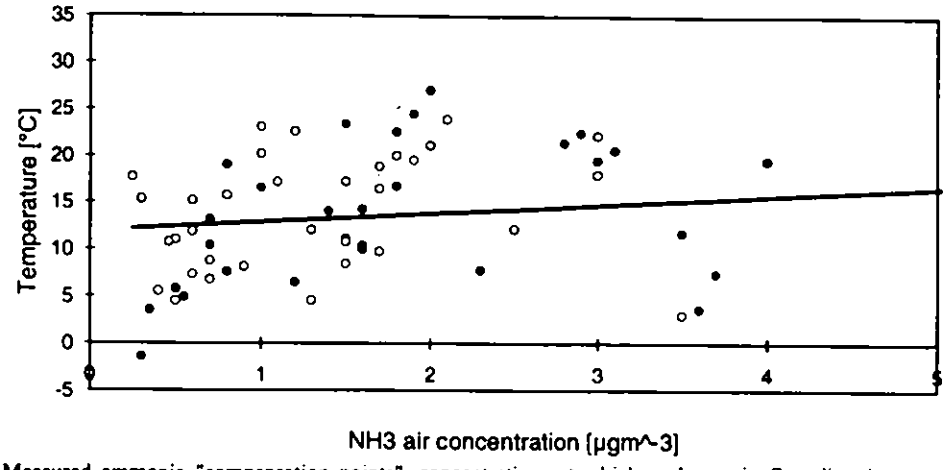

Fig.3: Measured ammonia "compensation points", concentrations at which a change in flux direction occurs, in relation to temperature. ●, Conditions from wet to dry; O, conditions from dry to wet. The line shown is combined regression line $T = (0.93 \pm 0.75)\, c + (11.95 \pm 7.03)$

wet annular denuders and subsequent NH_4^+ analysis is carried out in only one conductivity detector for all denuder liquids. The profile of wind velocity, air temperature and humidity were registered in six levels over ground. With this data set (time base half hourly mean values) deposition velocities and fluxes for NH_3 could be calculated /6/. The location of the measurement site in Germany is shown in Figure 1.

NH_3-gradient measurements reported here took place in the period from 22/03/1995 to 14/07/1995. An example for one day is plotted in Figure 2.

The flux calculation follows the procedure described in /7/. The vertical flux (F) is the product of the concentration (c) gradient with height (z) and the eddy diffusivity (K):

$$F = -K\, dc/dz \qquad (1)$$

Analogy of the mass flux to the transfer of momentum and heat is assumed:

$$F = -v_d c_z \qquad (2)$$
$$= -k^2 (z-d)^2 \frac{du}{dz}\frac{dc}{dz}(\Phi_p, \Phi_h, \Phi_c)^{-1}$$

The displacement height (d) is estimated from wind profiles during neutral conditions. k is the VON-KARMAN-constant (0.4). For the NH_3 concentration gradient and the wind velocity (u) profile, regression lines by the least square method are calculated. The empirical correction terms are calculated for unstable and stable atmospheric conditions using the RICHARDSON-number:

$$(\Phi_p, \Phi_h, \Phi_c)^{-1}_{unst} = (1 - 5Ri)^2 \qquad (3a)$$

$$(\Phi_p, \Phi_h, \Phi_c)^{-1}_{st} = (1 - 16Ri)^{3/4} \qquad (3b)$$

where:

$$Ri = g\frac{dT}{dz} \Big/ T\left(\frac{du}{dz}\right)^2 \qquad (4)$$

with $Ri > 0$ is stable and $Ri < 0$ is unstable. Neutral atmospherical conditions for the calculations here are considered as: $-0.03 < Ri < 0.03$.

The resulting canopy resistance (R_c) could be calculated after /1, 8/:

$$R_c = 1/v_d - (R_a + R_b) \qquad (5)$$

with the aerodynamic resistance R_a and the quasi-laminar layer resistance R_b as:

$$R_a = u / u_*^2 \qquad (6a)$$

$$R_b = 1/ku_* (Sc / Pr)^{2/3} \qquad (6b)$$

R_a is determined accurately for neutral and stable conditions in this way, and has been applied approximately for unstable conditions also. The friction velocity u_* is available from the wind profile, while the term with SCHMIDT and PRANDTL number $(Sc/Pr)^{2/3}$ yields 0.96 for NH_3.

3. RESULTS AND DISCUSSION

An NH_3 gradient dataset (three levels NH_3 concentration over grassland) for a time period of four months (completeness more than 70 %) was generated at the measurement place Melpitz. Both time periods with NH_3 deposition and NH_3 emission occurred. The NH_3 concentration and the change between deposition and exhalation are influenced by meteorological conditions. For this time period (22/3 to 14/7) all "compensation points" were plotted in Figure 3 as a function of temperature (0.5 m over ground), where the compensation point is found here as the concentration at which a change in the flux direction between level one and two occurred, using half hourly means of the database. For the compensation points a change from wet (deposition) to dry (emission) surface or vice versa was distinguished.

Figure 4 shows that the most "compensation points" exist in the concentration range from 0.5 to 2.0 µg m^{-3} (temperature range from 0 to 28 °C). These values are typical for an agricultural meadow with fertilization /9/. Some points are influenced by evaporation of NH_3 from water layers at the ground or plant surface during parallel water evaporation or condensation, especially during morning and evening time. The compensation points hardly increase with temperature.

The plot of NH_3-fluxes as a function of NH_3-concentrations for three example days (Figure 5) shows a compensation point in the same range as the derived "compensation points" from the flux direction change over the four months period of NH_3 flux measurements.

During these example days, typical fluxes and deposition velocities are calculated (with change in the direction) also. The typical resistances R_a and R_b are in the range of 10 to 100 s m^{-1}. For the surface

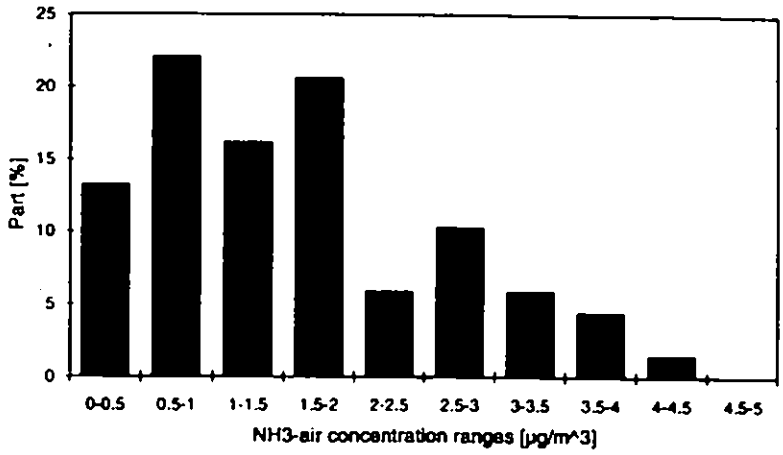

Fig. 4: Relative distribution of the "compensation points" from the measurements.

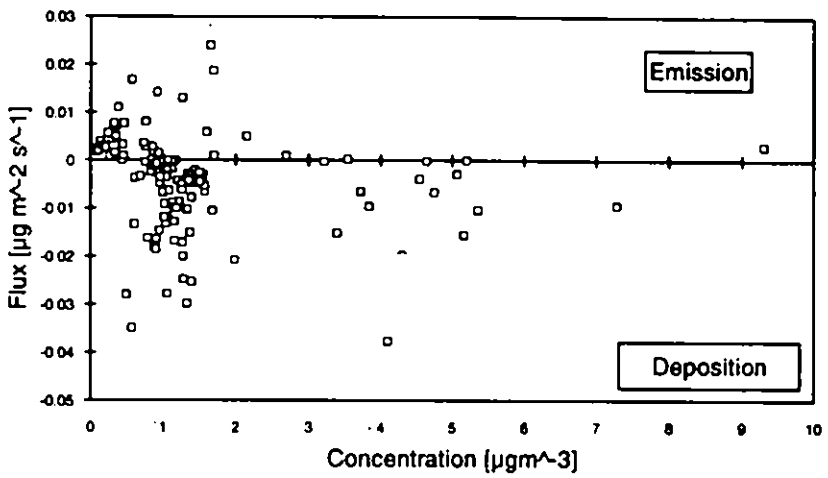

Fig. 5: NH_3-fluxes as a finction of ambient NH_3-concentration, showing results for 30/4/95, 6/5/95 and 7/5/95.

resistance (R_c), where deposition occurred the typical range is 100 to 300 s m^{-1}. For periods with emission, the calculations result in a quasi-negative canopy resistance, which is due to inappropriateness of the model. In this situation other parametrizations accounting for the surface concentrations are required.

ACKNOWLEDGEMENTS

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AN EXPERIMENTAL EVALUATION AND MODELLING OF AMMONIA SURFACE DEPOSITION FLUXES: MADRID CASE STUDY

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Abstract - This contribution presents the comparison between ammonia deposition fluxes measured by using the gradient method with modelled fluxes following the Sutton *et al.* (1993) bi-directional net flux model in the Madrid suburban area. Measurements of ammonia have been carried out by using an annular wet denuder developed by ECN (Holland). The system has three denuders at three levels (0.45, 1.20 and 3.30 m). A period of three days data is presented in this paper corresponding to 8-10 February, 1995. Net flux during this period is mostly downward. Stomatal and leaf fluxes are parameterized by following the Sutton and Fowler (1993) formulations. In addition, Wesely (1989) is implemented for stomatal resistance. Results of the comparison show a good agreement between measured and modelled fluxes a strong dependence on the relative humidity for the leaf fluxes is found.

1. INTRODUCTION

The exchange of gaseous ammonia between soils, waters, plants and the atmosphere is an important pathway in the terrestrial nitrogen cycle (Söderlund and Svenson, 1976). Quantification of ammonia (NH_3) exchange is a key component for air quality models and for formulating control policy for regional atmospheric pollutants. Ammonia deposition and emission is currently a subject of great interest. The interest has been stimulated by measurements showing very large rates of NH_3 deposition in moorland and forest (Duyzer *et al.*, 1992; Sutton *et al.*, 1993). The correct parameterization of the ammonia bi-directional fluxes is very important for air quality models. These models include the emission and deposition parameterization of many different substances such as ammonia. This parameterization is strongly dependent on land use. The air quality models have an important application over urban areas. The rate of deposition to semi-natural land in South European latitudes may be limited by substantial canopy resistance. In addition, there is the possibility that emission fluxes may also occur for some periods from these ecosystems. Although in north European ecosystems the net flux is still dominated be deposition in south European ecosystems the net direction of fluxes is not clear. Field experiments in south European ecosystems are necessary to test the validity of the resistance models on these ecosystems. The biosphere-atmosphere exchanges in the surface boundary layer depend on several factors, including the aerodynamic resistance to turbulent transfer between the vegetation of the soil and the atmosphere; the leaf boundary layer resistance, the stomatal resistance and other resistances, including the cuticular, mesophyll and soil resistances. An accurate evaluation of the ammonia surface resistances is important for the flux modelling.

In this contribution we present results of a short period of time on 8-10 February, 1995. In spite of this short period of time interesting results can be concluded. We have used the AMANDA annular wet denuder (Slanina *et al.*, 1994) to take ammonia concentrations at three different levels (0.45, 1.20 and 3.30 m in height). The AMANDA system has shown to be very reliable, although high manpower is required. We have used a net bi-directional net flux model although the net flux is downward during most of the period however a canopy compensation point must be calculated since emissions are clearly observed but not net emissions. The canopy compensation point approach accounts for the competition of both the bi-directional exchange through the stomata and the cuticular uptake. The canopy compensation point (χ_c) can be regarded as the net potential for ammonia exchange at the canopy level. In this bi-directional net flux model, the net flux above the canopy is divided into the bi-directional flux through the stomatal resistance (F_s) and the deposition flux to the leaf surface (F_w). Figure 1 shows a scheme of this model. The concentration at the leaf surface is assumed to be zero. The stomatal exchange is governed by the stomatal compensation point which is related to apoplastic NH_4^+ concentration and pH through the solubility equilibria.

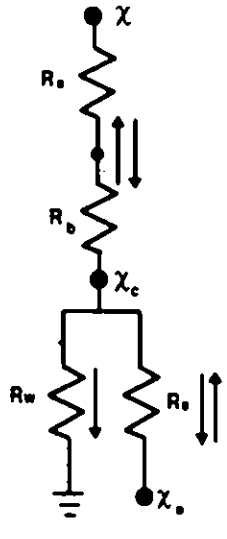

Figure 1. Bi-directional net flux model for ammonia.

2. EXPERIMENTAL

Ammonia net fluxes were measured by applying the aerodynamic method to a three level wet annular denuder system AMANDA developed by ECN (Holland). In addition, we used a sonic anemometer (5 m in height), a thermometer/hydrometer and a global radiation sensor.

The "Cuatro Vientos" Military Airport located in the south-west region of Madrid metropolitan area is the field experimental site (40°20' N, 3°51'10" W and 681 m above sea level). The terrain is semi-natural and the average roughness length is 2 cm. (San José *et al.*, 1985).

The denuders sample air at 30 l min^{-1}. The are rotating continuously and supplied with an acidic stripping solution ($NaHSO_4$, which collected NH_3 as NH_4^+ in the stripping solution), to a common detector for analysis. Analysis of the NH_4^+ is made in the system by membrane diffusion of NH_3 at high pH into a counter flow of deionized water, with a subsequent measurement of conductivity. Sampling is made every 120 seconds, 90 seconds are used to stabilize the signal and the last 30 seconds are used to perform the measurement.

Figure 2 shows the meteorological variables, turbulent parameters and sensible heat flux during the experimental period. Sensible heat flux is very small during the period except on the second day of experiment. Relative humidity at 2.5 m is very high and winds are reduced on the second part of the experiment. Turbulent stability is quasi-neutral during the first part of the period and stable and unstable periods are distinguished during the second and third day of the experiment.

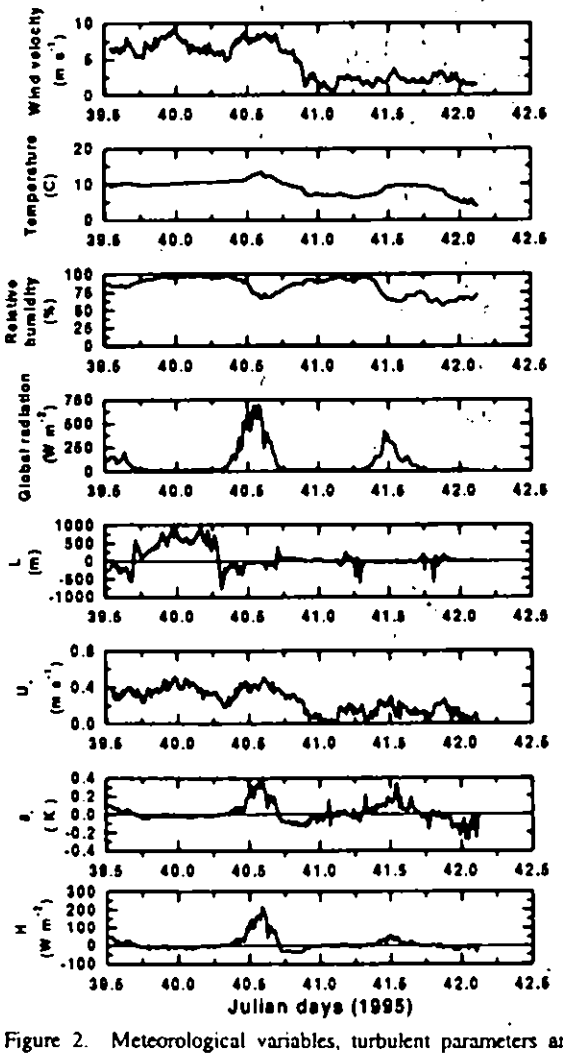

Figure 2. Meteorological variables, turbulent parameters and sensible heat flux during the three day experiment. L is Monin-Obokhov stability length; U_*, friction velocity; θ_*, friction temperature; H, sensible heat flux.

Figure 3 shows the ammonia concentrations at the three levels. The second part of the experiment shows an increase on the concentrations and fluxes.

3. BI-DIRECTIONAL NET FLUX MODEL

The sonic anemometer provides the sensible and momentum fluxes by eddy correlation method which is considered to be the "direct method". These fluxes are used to evaluate the Monin-Obykhov length which is incorporated in the integrated universal heat function Ψ_h. The aerodynamic method leads to the following concentration gradient at two different heights:

$$\chi(z_1)-\chi(z_2)=\frac{\chi_*}{k}[\ln(\frac{z_1-d}{z_2})-\Psi_h(\frac{z_1-d}{L})+\Psi_h(\frac{z_2}{L})] \quad (1)$$

χ_* is the scale ammonia concentration which is used to evaluate the ammonia flux:

$$F_{NH_3}=\chi_* u_* \quad (2)$$

This flux is considered the measured flux and we will compare the modelling results with these data. Sutton *et al.* (1993) model assumes that:

$$R_a(z)=\frac{1}{ku_*}[\ln(\frac{z-d}{z_0})-\Psi_h(\frac{z-d}{L})+\Psi_h(\frac{z_0}{L})] \quad (3)$$

$$R_b=\frac{2}{ku_*}[\frac{S_c}{P_r}]^{2/3} \quad (4)$$

The canopy compensation point can be evaluated by the following expression:

$$\chi_c=\frac{\chi_s R_w(R_a+R_b)+\chi[1m]R_w R_s}{R_w R_s+R_w(R_a+R_b)+R_s(R_a+R_b)} \quad (5)$$

R_w is parameterized following the Sutton and Fowler (1993) expression which depends on the relative humidity as follows:

$$R_w=\alpha\exp(\frac{100-rh}{b}) \quad (6)$$

Van Hove *et al.* (1989) found a strong increase in ammonia adsorption capacity of the cuticle between 45-95% relative humidity (rh). The values during this period were within this range so R_w is found to be very important for the net flux balance. The stomatal resistance is parameterized following the Hicks *et al.* (1987)

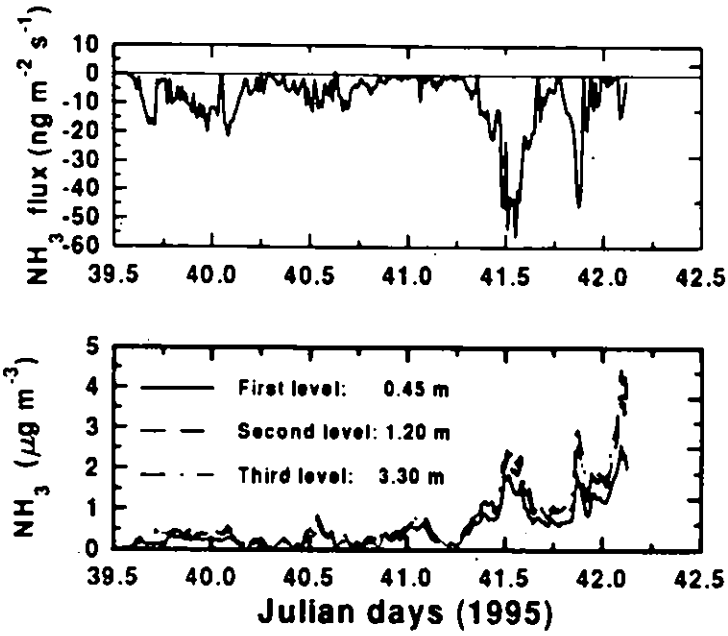

Figure 3 Ammonia concentrations and fluxes during the experiment.

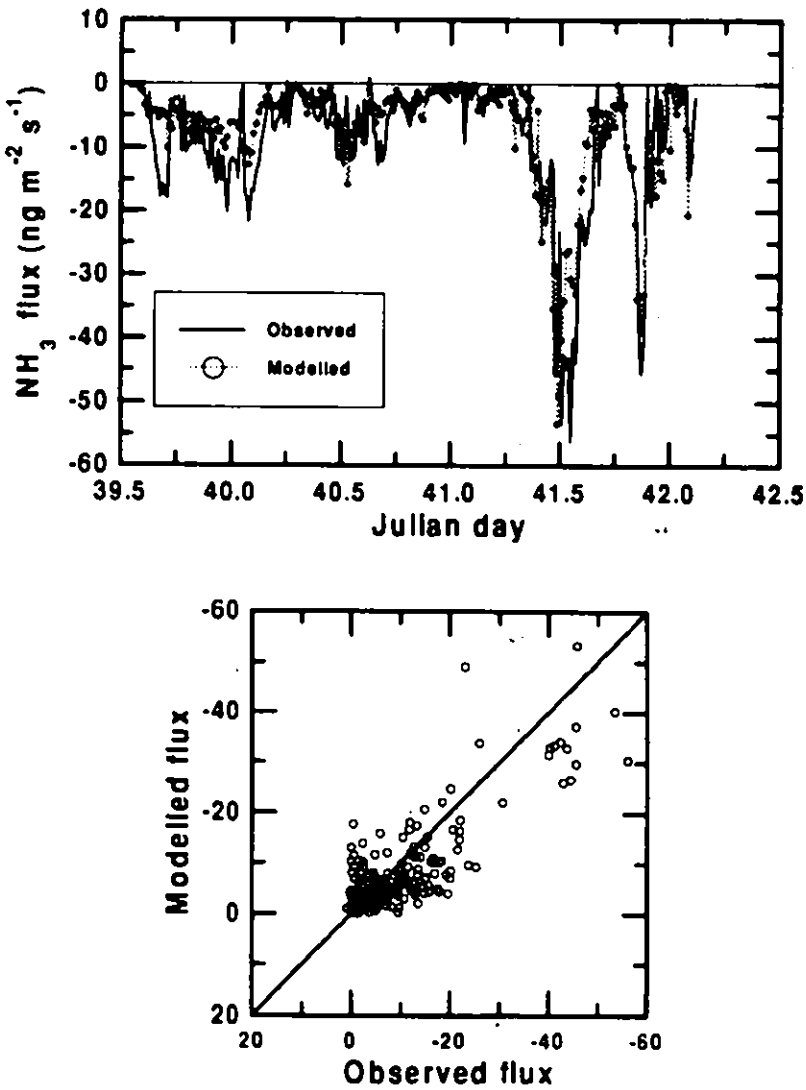

Figure 4. Comparison between ammonia measured (aerodynamic method) and the modelled fluxes (Sutton *et al.*, 1993).

expression:

$$R_s = c1(1 + c2/G) \quad (7)$$

where G is the solar radiation which is measured in our experiment. In addition, results were compared with those when stomatal resistance is parameterized following the Weseley (1989) expression:

$$R_s = R_i\left(\frac{200}{G+0.1}\right)^2 \left(\frac{400}{T(40-T)}\right) \quad (8)$$

where T is the surface air temperature. χ_s is the surface concentration which is non zero because of ammonia emission. We have used the expression given by Sutton *et al.* (1993) as follows:

$$\chi_s = \frac{c_1}{T} 10^{-\frac{c_2}{T}} \frac{[NH_4^+]}{[H^+]} \quad (9)$$

Figure 4 shows an excellent agreement between observed (aerodynamic method) and modelled fluxes (Sutton *et al.*, 1993). The correlation coefficient for the modelled versus observed fluxes is 0.66. If the Wesley (1989) parameterization is used for the stomatal resistance the comparison is slightly improved to 0.69. The R_i coefficient is 180. This is an average between the coefficients for agricultural land and range land for seasonal category 5 which corresponds to transitional spring with partially green short annual plants.

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THE CHEMICAL BEHAVIOUR AND DEPOSITION OF AMMONIA, AMMONIUM NITRATE AND NITRIC ACID

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Abstract–Turbulent fluxes of ammonia (NH_3) and nitric acid (HNO_3) were determined by the micrometeorological gradient technique over two different grassland sites (Saxonia, Upper Rhine Valley) during three field campaigns between 1991 and 1993. Ammonia was always deposited at both sites, NH_3 emission was only observed occasionally. Mean fluxes of both components were smaller at the Saxonian site, but the differences between both sites are not statistically significant. Despite extreme differences in soil moisture during the two campaigns in Saxonia, the mean fluxes are equal for both campaigns. The results were tested for the possibility of influences by chemical reactions between the two components and their particulate phase (ammonium nitrate; NH_4NO_3) by two methods. First, the characteristic time scale of the chemical reaction was compared with the characteristic time scale of the turbulent transport and second, the measured deposition velocity was compared with the upper theoretical limit of the deposition velocity.

INTRODUCTION

Dry deposition of gases and particles is an important sink for the atmosphere and a source for either nutrients or acids to the biosphere or the earth's surface. A well established method to measure surface fluxes of atmospheric trace substances is the micrometeorological gradient technique. However, a prerequisite for the applicability of the gradient technique is the 'constant flux approximation', which means that the fluxes have to be invariable with height. Through existence of chemical sources or sinks within the boundary layer this condition may not be met.

The system NH_3 - HNO_3 - NH_4NO_3 is known to be affected by reversible dissociation / association reactions which may be fast enough to influence the vertical gradients of these species. The governing chemical reactions of this nitrous triade are given by Stelson and Seinfeld (1982), as follows:

$$NH_3 + HNO_3 \rightleftharpoons NH_4NO_3$$

One method to test wether the influence of chemical reactions may change the surface fluxes significantly is to compare the transport time scale τ_t with the chemical reaction time scale τ_c. The constant flux approximation seems to be appropriate to provide reasonable flux results only when the species are chemically conservative ($\tau_c \gg \tau_t$) or always in equilibrium with their reactants ($\tau_c \ll \tau_t$).

During several field campaigns profile measurements were performed to determine the surface fluxes of ammonia and nitric acid by the micrometeorological gradient method. The presented results are derived from three campaigns (SANA* 1991, August 26 to September 10 and SANA 1993, September 14 to September 23, Melpitz near Leipzig (Saxonia); TRACT* 1992, September 7 to September 22, Bühl (Upper Rhine Valley)). The turbulent fluxes of NH_3 and HNO_3 calculated on the basis of the constant flux approach are shown. To test the possibility of flux divergences because of chemical reactions, the characteristic time scales for both, the chemical reactions and the diffusive transfer processes were calculated and a comparison between

* SANA: Scientific program accompanying the sanitation of the atmosphere over the new states of Germany
* TRACT: Transport of pollutants over complex terrain

the measured and the maximum deposition velocities are performed.

EXPERIMENTAL

Ammonia and nitric acid concentrations were measured on a mast in three heights. The measurement heights during SANA 1991 were 0.3 m, 1.5 m and 6 m, during TRACT 1992 they were 0.3 m, 5 m and 11 m and during SANA 1993 they were 0.5 m, 2.3 m and 10.5 m above ground. The vegetation at the sites was short grassland. In the time period of the SANA 1991 campaign the ground was extremely dry due to a precipitation deficit during the summer months, whereas in 1992 (TRACT campaign) and 1993 (SANA campaign) the ground was quite moist and the measurements had to be interrupted several times because of heavy rainfall. The NH_3 concentrations were measured with impregnated (oxalic acid) filters by the Institute for Analytical Chemistry of the Technical University of Vienna. For the determination of the HNO_3 concentrations the filter method described by Brunnemann et al. (1995) was used. During the SANA 1991 campaign ammonia concentrations were measured occasionally in one height only. Therefore fluxes of NH_3 could have not been calculated for this campaign.

Dry deposition analysis was performed on the basis of the constant flux approach and assuming that the gases are transported vertically by turbulent exchange similar to sensible heat. The relevant micrometeorological fluxes were determined by the eddy correlation method for the 1991 data and by the energy balance or modified bowen ratio method for the 1992 and 1993 data.

RESULTS AND DISCUSSION

Turbulent fluxes of ammonia and nitric acid are presented in figure 1. Positive values denote deposition, negative values are emission fluxes. A common feature of all plots is the large scatter of the data without any regular pattern. Mean values of NH_3 and HNO_3 fluxes are given in table 1. The large standard deviations reflect the high variability of the data. Mean NH_3 fluxes are positive, that means that deposition dominates. Despite the extremely different moisture conditions of the ground, the mean values of the turbulent fluxes of nitric acid are equal for the two SANA campaigns.

Tab.1: Mean NH_3 and HNO_3 fluxes and their standard deviations for the three different field campaigns

	NH_3 - flux [pptv m s^{-1}]	*HNO_3 - flux [pptv m s^{-1}]*
SANA 1991	—	8.4 ± 22.3
TRACT 1992	27 ± 69	15.3 ± 21.3
SANA 1993	6.5 ± 44	8.3 ±24.6

These fluxes were calculated assuming that the constant flux approximation is valid. As a first test of this assumption we took into the following considerations.

The thermodynamic conditions for the NH_3 - HNO_3 - NH_4NO_3 system during daytime mostly shifted the equilibrium towards the gaseous species (Seidl et al., 1995). The characteristic time τ_c for the gas phase to get into equilibrium with the particulate phase was calculated according to Wexler and Seinfeld (1990) for the two SANA campaigns. The results were compared with the characteristic times for the turbulent transport τ_t. The relation τ_t / τ_c is given in figure 2. Dlugi (1993) discussed that fluxes with τ_t / τ_c values in the range of 0.1 to 10 should be influenced by chemical reactions. The figure shows that most values of τ_t / τ_c are within this range. Only in the early morning and the evening hours the chemical reactions are very fast compared to the turbulent transport. Then the influence of chemical reactions on the turbulent fluxes should be negligible.

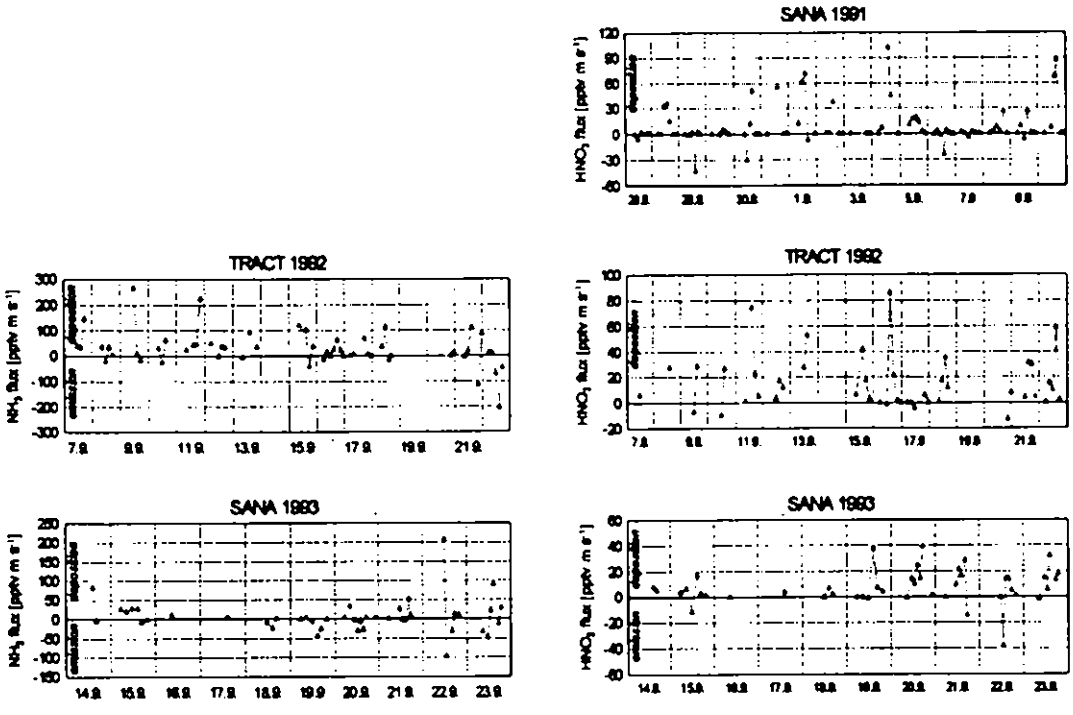

Fig.1: Turbulent fluxes of NH_3 and HNO_3 as measured during three different field experiments

Between Sptember 20 and September 22 in 1993 the ratios were about 1 during most of the day. These are certainly days when the constant flux approximation was not valid because of the chemical reactions.

Remarkably low values of τ_t/τ_c are observed during the SANA 1991 campaign between September 6 and September 9, in a time period when sea salt was advected and the concentrations of all components (gas phase and particle phase) were generally very low. In this time period turbulent transport was fast enough that the gradients were not affected by chemical reactions.

A second method to test the influences of chemical reactions was done by comparing the experimentally determined deposition velocities of HNO_3 with an upper theoretical limit of the deposition velocity which was defined as

$$v_{Dmax} = 1 / (r_t + r_{mt})$$

with r_t = turbulent resitance
r_{mt} = molecular turbulent resistance.

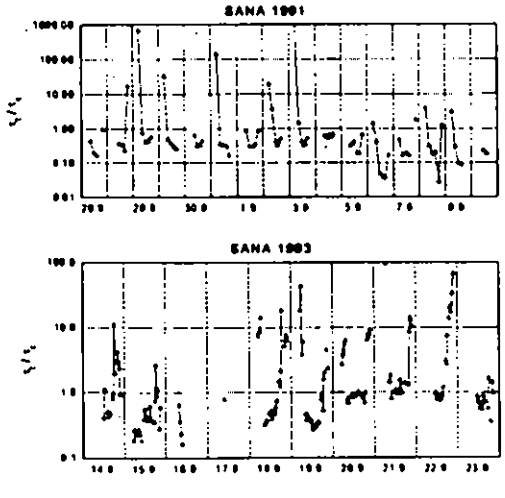

Fig.2: Ratio of turbulent transport time τ_t versus chemical reaction time τ_c.

This definition is based on the assumption that the canopy resistance is negligible for HNO_3. Measured fluxes of HNO_3 larger than the theoretical upper limit can be an indication for the influences of chemical reactions on the specific fluxes (e.g. Kramm and Dlugi, 1994). The results of this comparison is shown in figure 3.

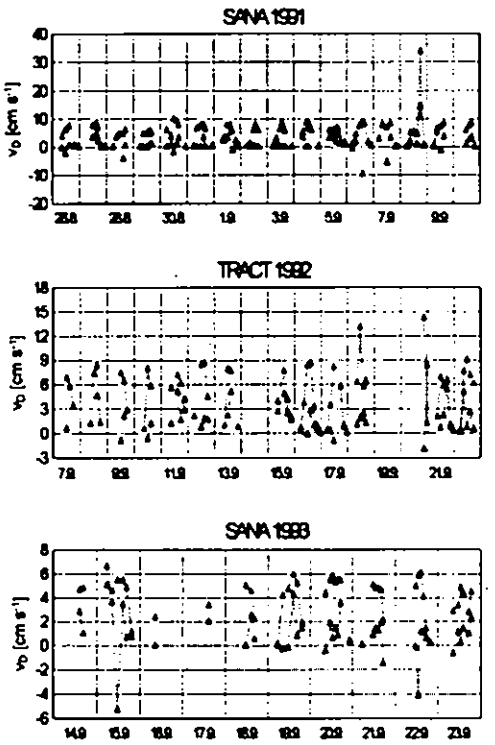

Fig.3: Comparison of measured deposition velocities of HNO_3 v_{Dexp} (open triangles) with calculated maximum deposition velocities v_{Dmax} (filled triangles).

During the all three campaigns the experimentally determined deposition velocities were smaller than the upper limit of v_D. That means that the comparison of the deposition velocities gives no hint on flux disturbances by chemical reactions.

The two methods used here to test the influence of chemical reactions show ambiguous results. From the ratios of chemical reaction times to turbulent transport times the influences of chemical reactions cannot be excluded most of the time but only in a very few cases, when the ratio is 1, the method gives a certain proof for disturbances of the constant flux layer by chemical reactions. The comparison of v_{Dexp} and v_{Dmax} never shows a definite influence of the chemical reactions, allthough it must be stated that this result is no proof for the absence of such influences.

The results of this work show that it is necessary to test the effects of chemical reactions on the constant flux layer in much more detail as could have been done here, because from the presented results such influences cannot be excluded in princible.

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Application of a NH_3 gas-to-particle conversion model to measurement data

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Summary

A dataset of simultaneous gradient measurements of gaseous NH_3, HNO_3, HCl and SO_2 together with particlulate NH_4^+, NO_3^-, Cl^- and SO_4^{2-} was used to investigate the quantitative effect of gas-to-particle conversion (GPC) on NH_3 flux measurements. The measurement data show periods of apparent NH_4^+ aerosol emission, as well as HNO_3 and HCl deposition with both $R_c>0$ and <0, indicating that GPC took place. From these data, input values at two heights were extracted and used in a numerical first-order-closure model. The model allows simultaneous treatment of the reaction of NH_3 with both HNO_3 and HCl. It also accounts for gradients of the dissociation constants, due to changes in temperature and relative humidity with height, and extrapolates the calculated profiles of concentrations and fluxes down to the surface. The model can simulate the observed phenomena quantitatively, but more measurement data of increased accuracy are necessary to enable statistically valid model assessments.

Introduction

Ammonia fluxes are usually measured by gradient techniques, which require the flux to be invariant within the height range in which the measurements are carried out. Over a homogeneous area a layer is expected to form in which fluxes are in equilibrium with the surface (e.g. Monteith and Unsworth, 1990). However, only fluxes of heat and chemically inert tracers are constant with height. Ammonia (NH_3) as the major atmospheric base reacts reversibly with nitric and hydrochloric acid forming ammonium aerosol and can also be neutralised by sulphuric acid. The reactions with HNO_3 and HCl may be given by:

$$\begin{aligned} NH_3 + HNO_3 &\xrightarrow{k_1} NH_4NO_3 \\ NH_4NO_3 &\xrightarrow{k'_1} NH_3 + HNO_3 \\ NH_3 + HCl &\xrightarrow{k_2} NH_4Cl \\ NH_4Cl &\xrightarrow{k'_2} NH_3 + HCl \end{aligned} \qquad (1)$$

where k_1, k_2, k'_1 and k'_2 represent the reaction rate coefficients. In dis-equilibrium situations this gas-to-particle conversion (GPC) can provide sources and sinks in the atmosphere resulting in height dependent fluxes and non log-linear concentration profiles of NH_3, acids and NH_4^+ aerosol. Where these reactions occur at rates similar to those of turbulent exchange, gradient techniques assuming a constant flux layer are, strictly speaking, not applicable for NH_3, as these methods would not derive the surface flux but a mean value for the flux in the height of the measurements (see Figure 1).

As the exchange of NH_3 is bi-directional and generally governed by an unknown canopy resistance (R_c) the fluxes of acids and NH_4^+ aerosol provide better means to detect GPC. HNO_3 and HCl can be expected to deposit with $R_c=0$ (e.g. Müller *et al.*, 1992) whereas particles in the prevailing size range of ammonium aerosol (0.01-0.1 mm) deposit with a deposition velocity (V_d) of about 1 mm s^{-1}. Significant deviation from the expected deposition velocities may be taken to indicate that GPC takes place. These deviations have been found during measurements (e.g. Huebert *et al.*, 1988; Sutton *et al.*, 1993; Zhang *et al.*, 1995).

The problem of the influence of GPC has been increasingly acknowledged over the past five years. The error that GPC induces for both individual NH_3 flux measurements and estimation of the net deposition/emission of NH_3 with ecosystems needs to be quantitatively assessed. GPC is also likely to effect the physical processes of the surface/atmosphere exchange themselves. For example, evaporation of particulate NH_4^+ into fast depositing gaseous NH_3 would potentially enhance the total deposition of reduced nitrogen in highly polluted areas. This would obviously have important consequences for the exceedance of critical loads of nitrogen. If NH_3 is emitted in the presence of a high background concentration of HNO_3, aerosol formation can deplete NH_3 near the surface resulting in bigger gradients and increased NH_3 emission. Although the produced NH_4^+ is expected to deposit mainly onto existing aerosol resulting in particle growth, the generation of new ultrafine NH_4^+ particles is also likely to occur.

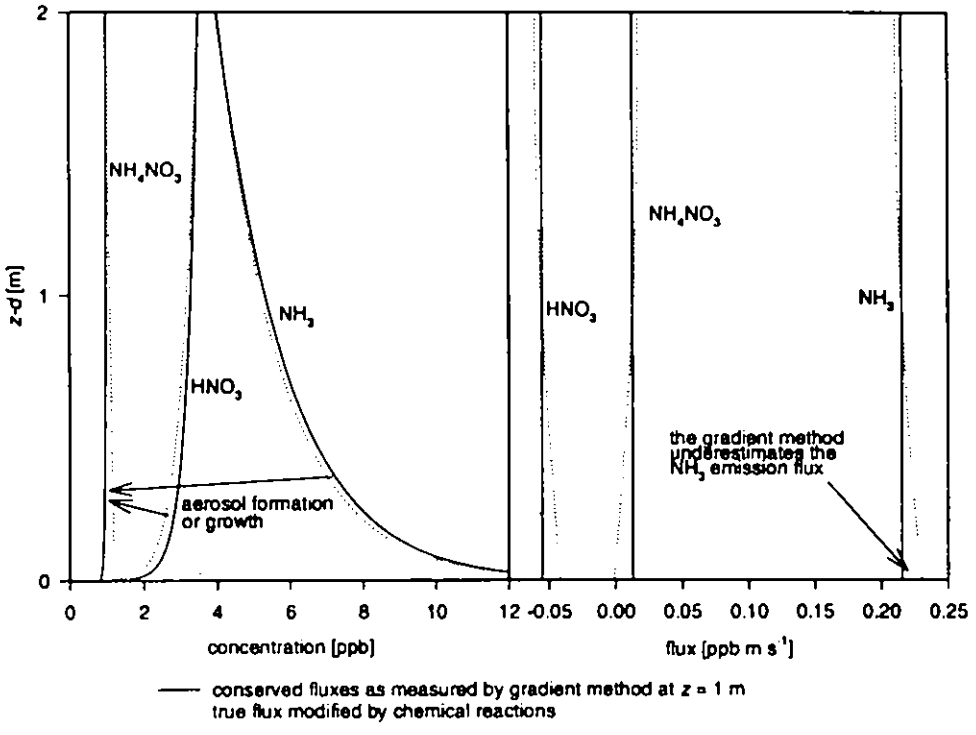

Figure 1. Schematic outline of the principle of gas-to-particle conversion. In this example, emission of NH_3 in the presence of a considerable HNO_3 concentration leads to formation or growth of NH_4^+ aerosol which is highest at the ground.

Field measurements

Unexpected surface exchange rates of gaseous HNO_3 and HCl as well as particulate NH_4^+ can be seen in previously unpublished data from measurements carried out in a joint field campaign in September 1989 as a part of the BIATEX project near Halvergate, Norfolk, UK. A site description of the experiment has been provided by Hargreaves *et al.* (1992) and Dollard *et al.* (1990). The data of four out of twelve runs are shown in Figure 2.

The average of the night-time runs (10 - 12) shows expected deposition fluxes for NH_4NO_3 and HNO_3 which indicate that GPC did not effect the NH_3 fluxes. In contrast, runs 1 and 5 show high apparent emission of NH_4^+ aerosol and deposition of HNO_3 and HCl faster than permitted by turbulence, $V_{max} = (R_a+R_b)^{-1}$, indicating aerosol formation or growth close to the surface. The opposite process, enhanced evaporation of aerosol near the surface, may be the cause of the apparently slow acid and too rapid NH_4^+ deposition in Run 8.

As the measurements included simultaneous gradients of NH_3, HNO_3, HCl, NH_4NO_3 and NH_4Cl they provide a unique dataset for model assessment. However, some other runs (data not included in Figure 2) show inconsistent data, e.g. deposition of all chemical species faster than permitted by turbulence, observation which cannot be explained in terms of GPC. A large contribution of SO_4^{2-} to the NH_4^+ concentration was also found during some runs requiring the inclusion of H_2SO_4 into the modelling which was beyond the scope of the first model tests presented here.

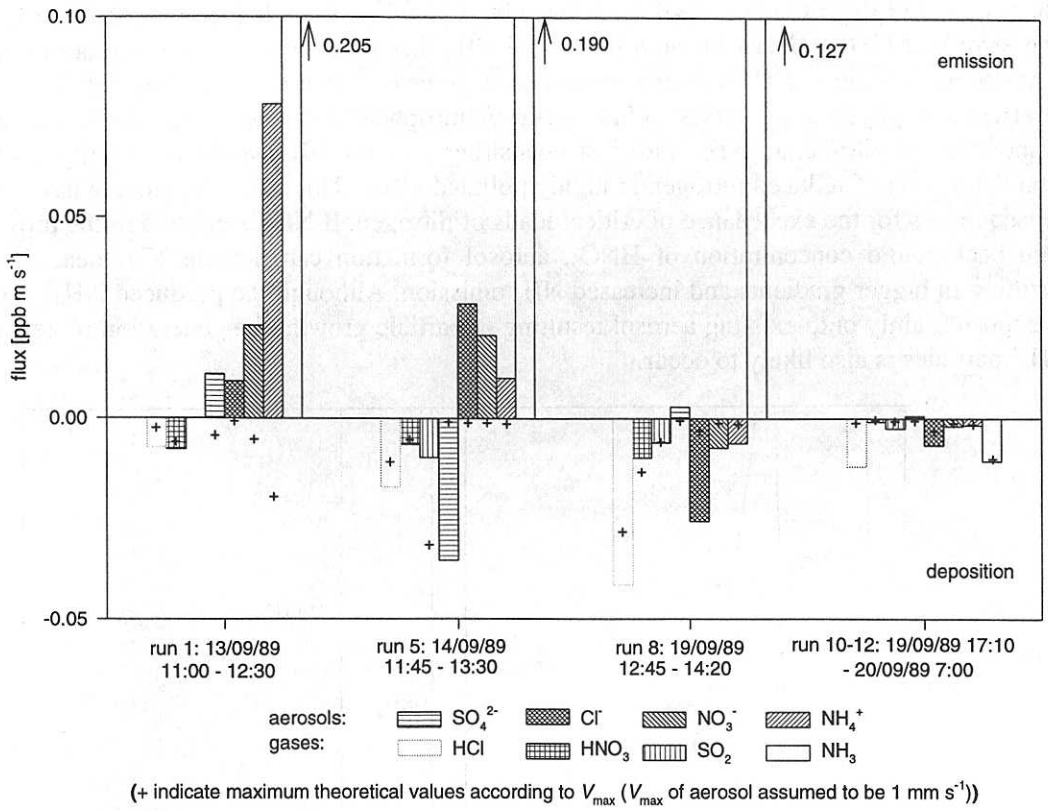

Figure 2. Fluxes of four out of twelve runs during the Halveragate '89 campaign as calculated with the aerodynamic gradient method (bars) and maximum deposition fluxes (+). Fluxes of both aerosol and acids show high deviation from the expected values.

The model

If the gradients of HNO_3 and NH_3 are obtained in the same way, i.e. if the concentrations are measured at the same heights, the error due to GPC for both fluxes should be expected to be similar, assuming the effect of HCl is negligible. Since the error in the HNO_3 flux can be estimated using the expected value for $V_d = V_{max}$ a first order correction of the NH_3 flux is given by:

$$F_{NH_3,real}(z_o') = F_{NH_3,meas}(1\,m) + \Delta F_{NH_3} \tag{2}$$

with

$$\Delta F_{NH_3} = [HNO_3]_{meas}(1\,m) \times \left(V_{d,HNO_3}(1\,m) - V_{max,HNO_3}(1\,m)\right) \tag{3}$$

Similar expressions can be derived for the correction for the reaction with HCl if appropriate. However, a potentially more accurate correction can be obtained by modelling the profiles of the concentrations and fluxes of the different chemical species. Here a first-order-closure model according to Brost *et al.* (1988), and also used by Kramm and Dlugi (1994), was applied. The divergence of the flux (F) with height (z) is given by the chemical source and sink term (Q):

$$\frac{\partial F_{NH_3}}{\partial z} = Q_{NH_3} \tag{4}$$

which for NH_3 can be written as

$$Q_{NH_3} = -[NH_3]\left(k_1[HNO_3] + k_2[HCl]\right) + \left(k_1'[NH_4NO_3] + k_2'[NH_4Cl]\right). \tag{5}$$

Closure of the model is provided by the classical flux gradient relationship:

$$F_{NH_3} = -K_H \frac{\partial[NH_3]}{\partial z}; \qquad K_H \approx \frac{z\kappa u_*}{\Phi_H\left(\frac{z}{L}\right)}. \tag{6}$$

Here K_H represents the eddy diffusivity; κ, the von Karman constant (0.41); u_*, the friction velocity, and $\Phi_H(z/L)$, the stability correction (Sutton *et al.*, 1993). Although K_H is modified in the presence of chemistry, Fitzjarrald and Lenschow (1983) found that the standard expression of equation (6) is a sufficiently accurate approximation. The equations of the form of equation (4) and (6) together with equation (5) form a set of three (five if the reaction with HCl is included) coupled second order differential equations which have to be solved simultaneously calculating the source/sink terms for each height after each iteration step. Here three features were added compared with the models of former authors:

1) The equilibria of NH_3 with both HNO_3 and HCl were dealt with simultaneously as some runs show a high contribution of NH_4Cl.

2) The dissociation constants of NH_4NO_3 and NH_4Cl (k_p), which form the link between k_1, k_1' and k_2, k_2', respectively, were calculated as functions of temperature and relative humidity. In this way the model is no longer limited to relative humidities below the deliquescence point and also allows vertical gradients of relative humidity and temperature to be accounted for. The expressions from Stelson and Seinfeld (1982) and Pio and Harrison (1987) were used to calculate the equilibrium constants.

3) Like for the model by Brost *et al.* (1988), the concentrations at two heights are required as input parameters. These were obtained by interpolating the measured gradients in order to account for scatter in the data. The model calculates the profiles between the two input heights. The values of the concentrations and fluxes at the lower boundary height were here used to extrapolate the profiles down to the surface, the roughness length (z_o), so that the surface fluxes can be found.

Results and discussion

The model described is applied to two different measurement examples as presented in Figures 3 and 4. Figure 3 shows a case in which the concentration product $[NH_3][HNO_3]$ does not obtain its theoretical value (k_p) at any height. This leads to aerosol evaporation which is highest close to the ground, where the HNO_3 concentration is smallest. The magnitude of the dis-equilibrium is governed by the concentration of HNO_3 rather than NH_3.

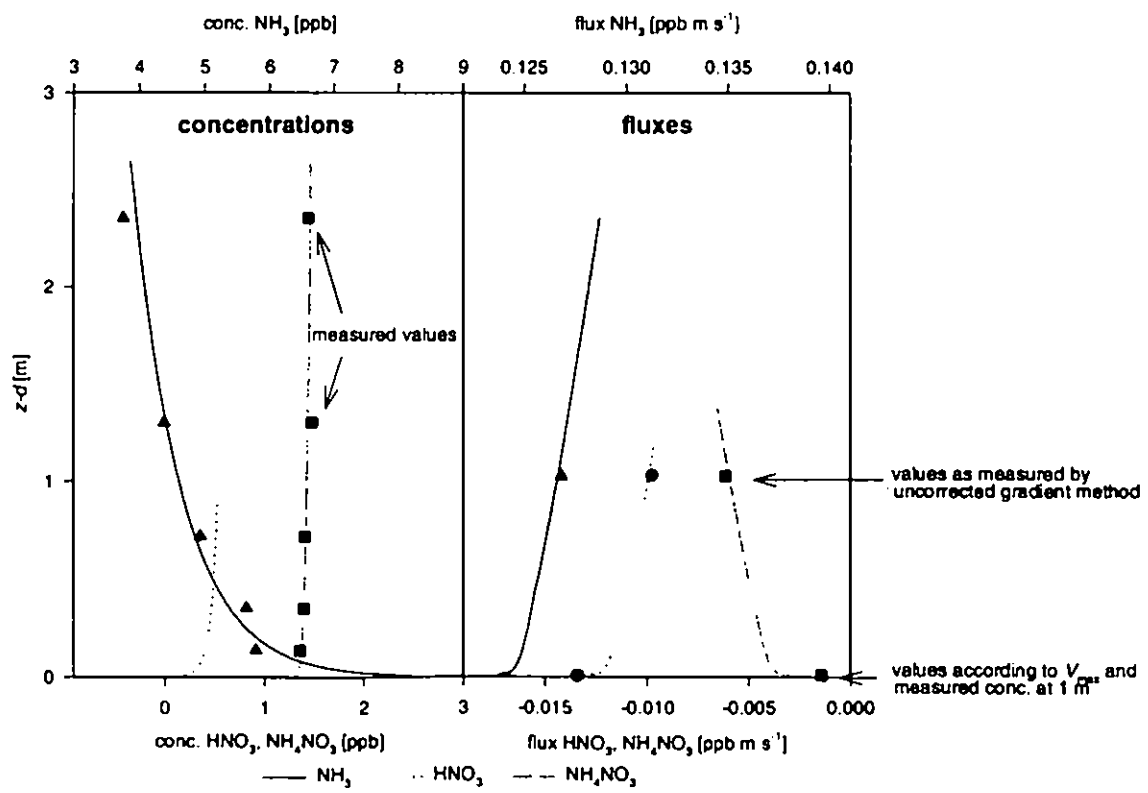

Figure 3. Model application to data from Halvergate, Run 8, when aerosol evaporation occurred close to the surface. The reaction with HCl is neglected as NH_4^+ and NO_3^- concentrations balance.

A comparison of the concentrations of the aerosol species suggested that for Run 8 the NH_4^+ is mainly present as NH_4NO_3. Hence the reaction with HCl was ignored. The high deposition velocity of the Cl^- aerosol could be explained by the chloride mainly consisting of sea salt which usually shows a larger mass median diameter than NH_4^+ aerosol leading to deposition faster than V_d = 1 mm s^{-1}

In contrast to Run 8, Figure 4 demonstrates the case of aerosol formation or growth which was more frequently observed during the Halvergate experiment, as shown for Run 5. In addition to gradients and fluxes Figure 4 also shows flux divergences (dF/dz), which vanish in equilibrium conditions (Kramm and Dlugi, 1994) and thus indicate the magnitude of the dis-equilibria. The relative humidity approaches 100% near the ground which leads to a small value of k_p. Because of the large emission of NH_3, the equilibrium product exceeds its theoretical value ($[NH_3][HNO_3]>k_p$) leading to aerosol formation or growth to be largest close to the surface, where the smallest value for k_p and the largest for $[NH_3]$ can be found. In order to balance the NH_4^+ concentration measured, the reaction with HCl has to be included in the model. As the NO_3^- and Cl^- gradient measurements show high scatter, the NH_4^+ gradients were used as input and arbitrarily split into NO_3^- and Cl^-.

In modelling both runs 8 and 5, the reaction rate coefficient, k_1 (and in Run 5 also k_2), was altered for the surface flux of HNO_3 (or HCl) to match the predicted value (see Figure 3), i.e. $-[HNO_3](z_o)/R_b$, with R_b being the resistance of the laminar boundary layer. A value of k_1 = 8 ppb^{-1} s^{-1} was found for Run 8 which results in a mean NH_4^+ formation rate of about 0.32 ng m^{-3} s^{-1}. The good match of the surface flux of the aerosol indicates data consistency (see Figure 3). However, matching the fluxes at z_o assumes no flux divergence to occur within the laminar boundary-layer. This assumption was also made by Kramm and Dlugi (1994), but becomes doubtful considering that in Run 8 the dis-equilibrium was largest near the ground.

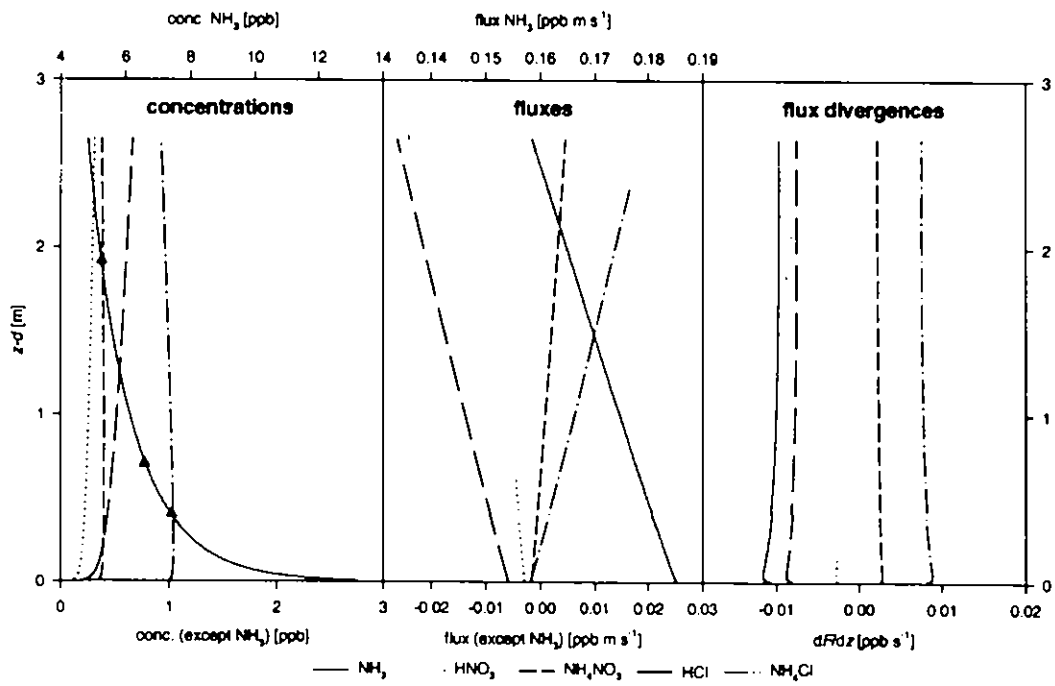

Figure 4. Model application to data from Halvergate, Run 5, showing aerosol evaporation close to the surface, including the reaction with HCl. The flux divergence is largest near the ground.

The numerical model can quantitatively simulate GPC for both aerosol production/growth and evaporation. However, not enough runs are available to enable a full model assessment. The profiles of Cl^- and NO_3^- showed too much scatter to be useful. These uncertainties give room for interpretation which was used to fit the models. Moreover, the values for the reaction rate coefficients have been chosen so as to fit the model results to the data.

For further model assessments it would be desirable to acquire more data of increased accuracy for the aerosol specication (i.e. NH_4NO_3, NH_4Cl). Recent developments of automated sampling techniques for all species under consideration (e.g. Wyers *et al.*, 1993; Khlystov *et al.*, 1995) should provide statistically valid input data. Temperature and relative humidity gradients have to be measured exactly in order to account for changes in k_p with height. The measurement of aerosol

size spectra at different heights could also provide a means to detect aerosol production and growth due to GPC.

More work is necessary to predict the kinetics of the equilibria from independent measurements, since the chemical time-scales are largely unknown. For example, the equilibrium products and reaction rate coefficients might be expected to change with aerosol size and composition. Furthermore, it has to be examined whether reactions within the quasi laminar sub-layer significantly contribute to the net effect of GPC. Quantification of these processes will allow improved correction procedures for gradient methods to be formulated providing more reliable estimates of the net effect of GPC.

Conclusions

The present analysis shows that gas-to-particle conversion (GPC) may have a substantial effect on the interpretation of flux-gradient measurements of NH_3. Examples of the measurements shown here are consistent with the occurrence of both aerosol evaporation and aerosol formation or growth. Aerosol evaporation at ground level may occur as a consequence of gaseous depletion due to dry deposition or positive relative humidity gradients, while aerosol formation or growth may result from NH_3 emission or negative relative humidity gradients. These processes may lead to both under- and over-estimation of NH_3 (as well as HNO_3, HCl) fluxes measured using classical gradient theory, and may be accounted for using the analysis presented here. GPC can also directly alter the rate of atmosphere/surface exchange, e.g. by transforming slowly depositing aerosol into fast depositing gaseous species and vice versa. Further development of the analysis will consider the need to treat reactions with acid sulphates, GPC processes within the viscous sub-layer and examine the reaction kinetics in more detail. This will be used to develop more general correction procedures as well as to assess the impacts of GPC on net fluxes with ecosystems.

Acknowledgements

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GAS DEPOSITION OF NITROGEN OXIDES ON THE TERRITORY OF THE CZECH REPUBLIC IN 1994

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Abstract-In this communication detailed map of the dry deposition of nitrogen oxides is presented for the territory of the Czech Republic in 1994. The deposition values have been calculated for a rectangular grid-squares of 10 x 10 km. Daily concentrations of NO_x at ground level had been measured at 172 monitoring stations situated unevenly over the territory of the Czech Republic. In the areas where concentration data were not available, the values have been computed by spatial interpolation based on linear Kriging. The deposition was calculated from these air concentrations using deposition velocity information on land-use types, on atmospheric wind speed and stability and on dry deposition rates from published studies. Using a literature review of observations, estimates of the surface resistance for NO_x are made. These are combined with the aerodynamic resistance and the boundary layer resistance calculated from boundary layer theory and meteorological data to yield an estimate of the yearly mean deposition velocity for each surface type in the land-use data base. This then enables one to calculate the areally-weighted yearly mean deposition velocity of NO_x. The spatial variation of NO_x deposition velocity is reported. It is lower than 2.2 $mm.s^{-1}$ to agricultural land and greater than 3.5 $mm.s^{-1}$ to forests.

Key word index : Dry deposition, deposition velocity, resistance analog, land-use type, nitrogen oxides, Kriging.

1. INTRODUCTION

The Czech Republic decided in 1992 to participate in the UN ECE mapping program for critical loads and critical levels. One aim of the National program is the calculation of deposition and its geographic variation by means of thematic maps. These can then be compared with critical load maps to deduce exceedance. A great variability in deposition across a heterogenous landscape as well as variability of ecosystem sensitivity made the critical loads to be compared with the actual deposition values in a grid-squares 10 x 10 km.

The most common way of parameterizing experimental results and of simulating dry deposition in models is by using the concept of deposition velocity V_z. It is defined as follows (Voldner et al., 1986):

$$F = V_z C_z \,. \tag{1}$$

F is the flux of pollutants to unit area of ground and C_z is the concentration of pollutant at a height z above the surface. Processes of dry deposition are conveniently represented in terms of a resistance analog in which the inverse of V_z called the total resistance to pollutant transfer (r_t) is given by:

$$r_t = r_a + r_b + r_s \tag{2}$$

where

r_a is the aerodynamic resistance associated with turbulent transfer across the atmospheric boundary layer,

r_b is an additional resistance that account for pollutant transfer across a quasi-laminar layer adjacent to the surface,

r_s is the surface resistance associated with pollutant-surface interaction.

2. DEPOSITION VELOCITY AND RESISTANCE TO TRANSPORT

The theoretical backround is described in Voldner et al. (1986) and will be summarized for the Czech Republic situation bellow. The aerodynamic resistance r_a was calculated using the micrometeorological relationship of Wesely and Hicks (1977) and Sheih et al. (1979). For deposition of gases to land and frozen surfaces

$$r_a=[ln(z/z_o)-\psi_c]/ku_* \tag{3}$$

where

$$u_*=ku_z/[ln(z/z_o)-\psi_m]. \tag{4}$$

For deposition of gases to water

$$r_a + r_b=[ln(ku_*z/D) -\psi_c]/ku_*. \tag{5}$$

D is the molecular diffusivity of the gas, k is the von Karman constant (0.4), u_* is the friction velocity, u_z is the mean horizontal wind speed at height z above the zero place displacement height, z_o is the surface roughness and ψ_m, ψ_c are stability correction functions for momentum and pollutant, respectively. For stable conditions ($0<z/L<1$) ψ_m and ψ_c are given by the following equation:

$$\psi_m = \psi_c = -5\ z/L \tag{6}$$

L is the Monin-Obukov length.

For gaseous deposition to surfaces other than snow or water, we have calculated the boundary layer resistance r_b using the empirical relationship suggested by Wesely and Hicks (1977) and Hicks (1984) as follows:

$$r_b=5\ Sc^{2/3}/u_* \tag{7}$$

where Sc is the Schmidt number (the ratio of kinematic viscosity of air to the molecular diffusivity of the gas). For NO_x Sc of 1.07 was used by Hicks et al.(1987).

Information on r_a, r_b, r_s as a function of meteorological parameters and surface type for circular region 30 km in radius around the choiced 32 meteorological stations situated evenly over the territory of the Czech Republic was extrapolated to each grid-square 10 x 10 km. Annual harmonic mean of the surface resistance r_s and the surface roughness z_o for gas NO_x was calculated from season data published by Voldner et al.(1986) and this was used for each surface (Table 1). Over water bodies, z_o is calculated from the following equation:

$$z_o=\gamma(9.1u_*)+0.016u_*^2/g \tag{8}$$

where γ is the kinematic viscosity of air and g the acceleration due to gravity.

Table 1. Yearly harmonic mean of the resistance r_s (s cm^{-1}) and the surface roughness z_o (cm) for NOx* for each surface type

Surface type	Surface resistance r_s	Surface roughness z_o
Coniferous forest	2.11	90
Deciduous forest	3.2	90
Agricultural land	5.49	0.08
Grassland	4.16	0.08
Urban	10	100
Open water	70	+

* NO and NO_2

+ Calculated from Equations (4), (6) and (8).

For stable atmospheric conditions associated yearly mean horizontal wind speed u_z was calculated from values measured at the choiced 32 meteorological stations. Yearly mean u_z was derived from long-termed measurements published in the Atlas of the Climate of the ČSSR (IH, 1960). Yearly mean V_z at 10 m reference height for each surface type was calculated from the Equation (2). r_a was obtained from Equations (3)-(6) using harmonic mean z_o from Table 1 and an appropriate L and u_z for the stable conditions. r_b was calculated for gas NO_x from Equation (7). Harmonic mean r_s was selected from Table 1.

3. CALCULATION OF GAS DEPOSITION OF NITROGEN OXIDES

Daily concentrations of NO_x (the sum of NO and NO_2) were measured at a height of 2 m at 172 monitoring stations situated unevenly over the territory of the Czech Republic using spectrophotometric method of determination (CzIH, 1995). In the areas where concentration data were not available, the values have been computed by spatial interpolation based on linear Kriging (Zapletal, 1994). On the basis of daily measurements at these stations in the year 1994 the yearly means air concentration C_z were calculated. For a given surface yearly dry deposition D is calculated as the product of the yearly mean air concentration C_z, the yearly mean dry deposition velocity V_z and the time T The yearly-mean areal-average D_{ar} to a grid-square 10 x 10 km is the product of the yearly mean concentration C_z, the areal mean yearly dry deposition velocity V_{ar} and T. V_{ar} was calculated for each grid-square 10 x 10 km by weighting the values according to fractional surface coverage (grid-square 1x1 km).

4. RESULTS AND CONCLUSIONS

The land-use data base was derived from the map "Land use" (IGCAS, 1992). A single land-use type was defined for each 1x1 km grid-square according to the dominant (i.e. most prevalent) land-use in that square. The land-use types used include coniferous forest, deciduous forest, mixed forest, agricultural land, grassland, mining and devastated areas, urban areas and open water. In the middle Bohemia and middle and south parts of the

Moravia dominate agricultural activities, the forest is dominant on the frontier of the country.

The dry deposition velocity field of NO_x for 1994 is shown in Figure 1 with a spatial resolution of 10 x 10 km. The average deposition velocity across the country is equal to 2.8 $mm.s^{-1}$. The highest dry deposition velocities are found over the forests and they reach average values above 3.5 $mm.s^{-1}$, because aerodynamically controlled resistance is not dominant over the forests. The average deposition velocity to agricultural land was equal to 2.2 $mm.s^{-1}$ and to grassland, where aerodynamic resistance cannot be ignored, was equal to 1.5 $mm.s^{-1}$.

In Figure 2 the yearly mean gaseous NO_x deposition is presented for the Czech Republic with a spatial resolution of 10 x 10 km. The top 5% of values of gas NO_x deposition (>750 eq $H^+.ha^{-1}.a^{-1}$) was found in north-west part of the Bohemia, in north-east and south-east Moravia and in the greatest cities. This is consistent with highest air concentration values of NO_x. The 5% share of lowest values (<100 eq $H^+.ha^{-1}.a^{-1}$) are located in the region of south Bohemia and in area of north-east Moravia. The yearly mean value of gaseous NO_x deposition in the year 1994 was 406 eq $H^+.ha^{-1}.a^{-1}$. The range of gas NO_x deposition values is 1192 eq $H^+.ha^{-1}.a^{-1}$ (min=30 eq H^+. $ha^{-1}.a^{-1}$, median=410 eq $H^+.ha^{-1}.a^{-1}$, max=1222 eq $H^+.ha^{-1}.a^{-1}$).

The numeric results of the calculations have been classified into 9 categories for the purpose of the cartographic displaying. For better orientation each map is supplemented with the frontier of the Czech Republic and the EMEP grid (size 150 x 150 km), which is the spatial reference for the European maps used within UN ECE (CCE, 1991).

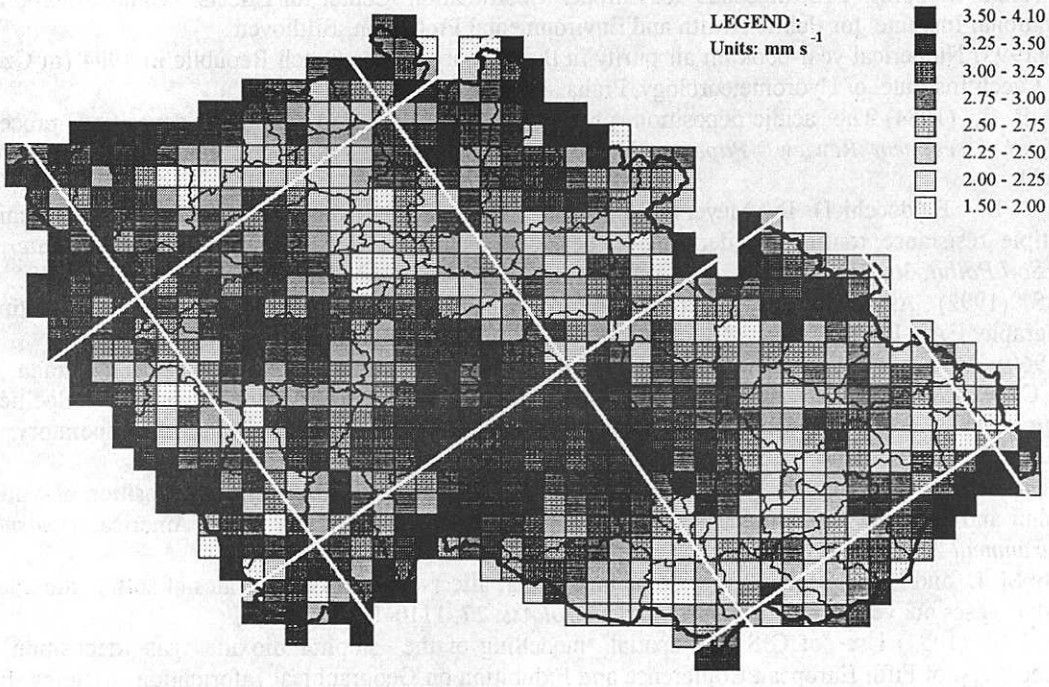

Fig. 1. Dry deposition velocity field of NO_x for 1994 ($mm.s^{-1}$).

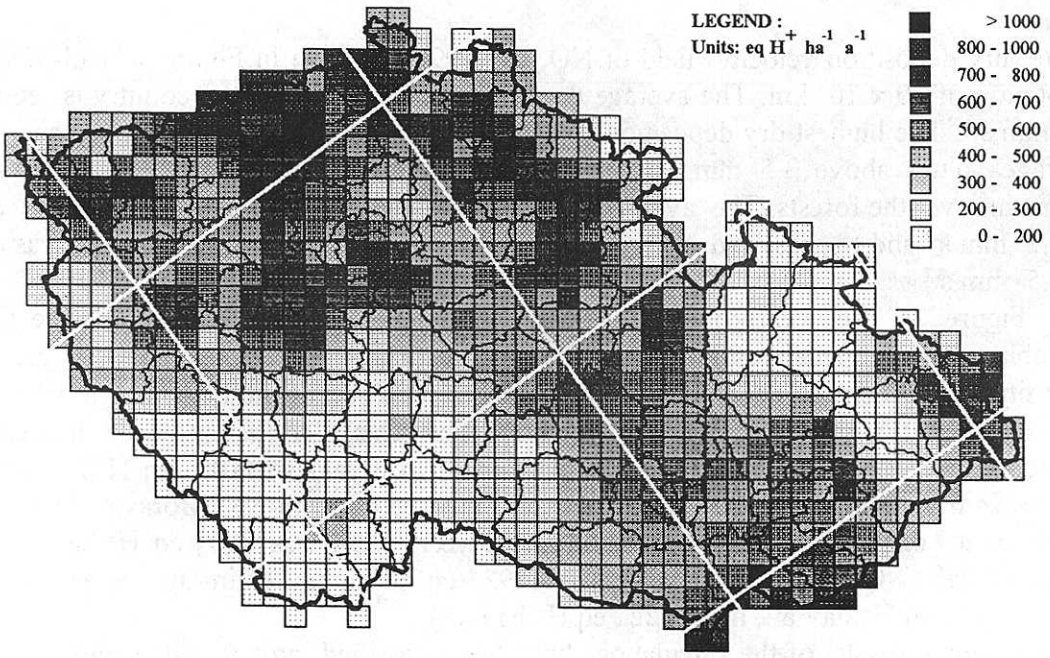

Fig. 2. Gas deposition of NO_x in the Czech Republic in 1994 (eq $H^+.ha^{-1}.a^{-1}$).

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NUTRIENTS AND GROWTH OF FOREST TREES AS AFFECTED BY NITROGEN DEPOSITION

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Abstract - Over 9 years, research with special emphasis on forest-ecosystems and nitrogen (N) was carried out in a Douglas fir stand to estimate levels and effects of air pollution as part of the Dutch National Programme on Acidification. Needle N increased to values indicating N-saturation. At the same time, arginine-N increased, which is a N storage compound typical for conifers. Needle K and P and their ratio to N, however, changed to values considered as growth-limiting. Nevertheless, the forest was qualified as highly productive, as compared to similar forests with much lower N deposition, and as compared to Dutch yield tables for Douglas fir. Biomass partitioning was changed: the LAI and S/R ratio were high and root biomass was low, suggesting increasing the sensitivity to drought, frost and wind throw. Reduction in the N deposition to the forest floor, results in a rapid decrease in N in the soil solution. Although arginine-N decreased from the first year on, total N and also tree growth were not affected by the treatment. The slower response of the trees might be due to the large N buffering capacity and to foliar uptake and/or reallocation of N. In a similar experiment in an area with higher N deposition and where tree growth is reduced, a reduction in N deposition led to growth improvement which was inversely correlated with decreases in needle arginine-N. We therefore expect that, when N deposition is not changed, the mineral condition of the trees in Speuld will continue to deteriorate. This will be reflected in an increasing shortage of K and P and a continued increase in N and arginine, which will lead to growth reduction within a few years time.

Keywords: Arginine, S/R ratio, partitioning, nutrients

1. INTRODUCTION

The current estimation of the mean nitrogen load in the Netherlands is 2750 mol ha^{-1} yr^{-1}, of which 73% is NH_x and 27% is NO_y. Agriculture is the largest Dutch contributor to NH_x (90%), and traffic (75%) to NO_y deposition (Erisman & Draaijers, 1995). Regional deposition can be very different, and in areas with intensive livestock farming forests may be exposed to higher deposition rates. Long-term increased atmospheric input of N may dramatically change forest ecosystems by acidification and/or eutrophication. Prominent changes to the non-tree part of the ecosystem are the increasing number of nitrophilous species in forest undergrowth (Van Dobben *et al.*, 1994) and the decline in the number of fruiting bodies of ectomycorrhizal fungi (Arnolds, 1991). In trees, nutritional imbalances may result from the loss of base cations from the soil, from preferential uptake of NH_4^+ by roots and from competition between NH_4^+ and the uptake of cations like K^+, Mg^{2+} and Ca^{2+} (Boxman *et al.*, 1995). Next to these soil mediated effects, N may be taken up directly by the foliage, resulting in increased N concentrations and disturbing the N allocation in the tree. Eutrophication by N will influence tree growth and change biomass partitioning in trees. The present investigation was aimed at assessing the impact of N containing air pollution on forest trees under ambient conditions and at assessing effects and reversibility of a reduction in that atmospheric input.

2. MATERIALS AND METHODS

The Speuld site covers 2.5 ha, was planted with 2-year-old Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco L.; Arlington) in 1962 and is located in a large forested area in the Netherlands. The canopy is closed, stem density is 800, average diameter at breast height (DBH) is 0.254 m and average tree height is 22.2 m (Jans *et al.*, 1994). The site is surrounded by deciduous and coniferous species, located on top of an ice-pushed ridge and the soil is classified as Orthic- or Holtpodzol. The climate is moderately humid, the groundwater table is at 40 m depth, sources of NO_x are located to the south-east (Ruhr area) and to the south-west (Rotterdam port), and sources of NH_3 are located within a few km to the south and to the north of the stand. Tree growth and architecture was assessed each year (1986-1993) as described by Jans *et al.* (1994). Needle nutrient concentrations were determined yearly (Steingröver & Jans, 1995). In 1989 a manipulation experiment was set up. Underneath a transparent roof (below the tree crowns), two plots (10 m x 10 m) were designed to receive either clean water (roof-clean plot) or ambient throughfall (roof-control plot). The roof-clean plot received water in mineral composition comparable to throughfall, except for N and S, which were excluded. The roof-control plot received original throughfall water caught on the roof surface. A detailed description has been given elsewhere (Boxman *et al.*, 1995).

3. RESULTS AND DISCUSSION

3.1 Nutrient relations and biomass partitioning

The criteria developed by Van Den Burg (1988) to describe the nutrient condition of Dutch Douglas fir trees, based on tree biomass production, were used to judge the nutrient concentration. The mineral condition of the trees was far from optimal and in fact deteriorating with time: P was constantly deficient and K decreased below deficiency levels (Table 1). The N concentration, however, increased to values higher than strictly needed for biomass production. This increase was associated by an increase in arginine-N (from 22 to 57 μmol g^{-1} between 1989-1994), a storage compound with a low C/N ratio and typical to conifers (Table 3). The increasing imbalance

Table 1: Average nutrient concentration in Speuld (% DW), compared to Dutch criteria for Douglas fir (after Van Den Burg, 1988).

		N	P	K	Ca	Mg	N/P	M/K	N/Mg
Speuld in 1987		1.75	0.09	0.62	0.36	0.08	19	2.8	22
Speuld in 1993		1.98	0.10	0.54	0.33	0.09	20	3.7	22
Criteria:	Deficient	<1.40	<0.14	<0.60	<0.25	<0.07	>17	>4	>17
	Sufficient	1.4-1.8	0.14-0.2	0.6-0.8	>0.25	0.07-0.1	17-10	4-2	17-10
	Optimal	1.8-2.5	>0.22	>0.8		>0.1	<10	<2	<10

was also reflected by the changes in the N/P and N/Mg ratio's to values considered to be growth limiting.

Despite all nutrient deficiencies Speuld is growing well and faster (26 m^3 ha^{-1}) then predicted on basis of yield tables (15 m^3 ha^{-1}) for Dutch Douglas fir (La Bastide & Faber, 1972). This is despite the fact that the last thinning, normally applied every 5-7 years to increase tree growth space, was in 1984. These tables are based on data collected in the early seventies and N input has increased considerably since then (Erisman & Draaijers, 1995), implying that they are no longer valid in the present situation. Biomass partitioning was also altered by the high N input: compared to productive and fast growing stands in areas with a lower N deposition the shoot:root S/R) ratio was twice as high (Keyes & Grier, 1981; Espinosa, Bancalari & Oerry, 1987). The high S/R ratio reflected a high leaf area index (LAI 12.4) and a low amount of root biomass. This will almost certainly increase the sensitivity of the trees to drought, frost and wind throw. In conclusion, it may be said that the high N input over the last decades has resulted in an increased productivity, altered biomass, partitioning and increased sensitivity of the trees in Speuld. The discrepancy between growth limiting levels of nutrients on one hand and growth stimulation on the other is obvious, and is probably caused by the fact that these (nutrient) criteria only apply in situations when N is growth limiting, which is no longer valid in the present situation.

3.2 Effects of reducing the N deposition

The mean N deposition flux to Speuld was 3500 mol ha^{-1} yr^{-1} (2600 mol NH_4^+-N, 900 mol NO_3^--N). According to Aber *et al.* (1989) the Speuld ecosystem is N-saturated: availability of inorganic N is in excess of total plant and microbial demand and N is leaving the ecosystem in the leachate at a depth of 0.9 m. The N deposition was reduced to less than 400 mol ha^{-1} yr^{-1} in the manipulation experiment and the inorganic N in the soil solution responded within one year. NH_4^+ dominated over NO_3^- in throughfall, but in the soil solution the reverse was true due to nitrification, preferential uptake of NH_4^+ by roots or by immobilization. The leaching of N from the ecosystem decreased significantly to values even below the target level of 400 μmol l^{-1} for groundwater. The leaching of the accompanying cations (Al^{3+}, Mg^{2+}, Ca^{2+} and K^+) was also reduced (Boxman *et al.*, 1995), implying a very tight input-output coupling. The N-cycle in the roof-clean plot changed from an open to a more closed one, indicating reversibility of the N-saturation, although the soil still contains a large amount of immobilized N and it is therefore uncertain what will happen with this N in the future. The total N concentration of the needles was not affected by the treatment. The arginine concentration, however, decreased from 26 to 9 μmol g^{-1} between 1989 and 1994, whereas in the ambient control the concentration increased from 22 to 57 μmol g^{-1}. The slower response of the trees is probably due to a large buffering capacity and to reallocation and/or to foliar uptake of N. A similar manipulation experiment was performed in an area with higher N deposition (Usselstein) and with decreased tree growth. In this case reduction of the N deposition lead to growth improvement and to reductions in total needle N after 2-3 years (Boxman *et al.*, 1995).

We therefore expect that the reduction in N deposition in Speuld will eventually also lead to decreases in total needle N and to improvement of the mineral balance of the trees. If N deposition is not changed however, the mineral condition of the trees will continue to deteriorate, reflected in increasing amounts of N and arginine-N and in an increasing shortage of other nutrients. This will eventually lead to growth reduction.

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LONG-TERM RESPONSES OF SMALL-SCALE AQUATIC SYSTEMS TO REDUCED ATMOSPHERIC AMMONIUM AND SULPHATE DEPOSITION

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Abstract: Seven small-scale indoor ecosystems, simulating hydrologically isolated soft waters, were exposed to different artificial rain solutions during a 2-year period, and later on to a 10-year period of clean, artificial rain water. Two major types of rain water were used: water with sulphuric acid (pH 5.6-3.5) and water with ammonium sulphate (pH 5.6). The treatments with ammonium sulphate, particularly, caused acidification up to pH 3.5 as a consequence of nitrification of ammonium. This acidification led to increased levels of Ca, Mg, Mn, Al, Cd and Zn in the water layer. Typical plants of soft waters declined and were overgrown by *Sphagnum* species and *Juncus bulbosus*.

A slow but gradual recovery to the pre-treatment water chemistry was observed during a 10-year period of treatment with clean, artificial rain. The species composition in the small-scale ecosystems which were treated with sulphuric acid, did not differ from the control, although the abundances of *Juncus bulbosus*, *Hydrocotyle vulgaris* and *Sphagnum* species were still higher after 10 years. The recovery of the water quality was less distinct in the small-scale systems treated with ammonium sulphate. In these systems almost all plants of soft-water communities had disappeared in the first few years following the ammonium sulphate application. After 10 years of clean rain treatment *Sphagnum* species were still very abundant and the water volume strongly reduced because of the luxurious growth of *Molinia caerulea* and *Juncus effusus*.

It is concluded that the recovery of the water chemistry and the vegetation in soft-water ecosystems is very slow after ammonium sulphate addition, compared with the recovery after sulphuric acid treatment.

1. INTRODUCTION

During the last decades it has become clear that atmospheric nitrogen deposition is an important contributant to the decline of sensitive ecosystems. Critical loads for nitrogen deposition are especially low for shallow soft-water lakes (Bobbink *et al.*, 1992). Almost all acid-sensitive macrophytes of oligotrophic soft-water lakes have become rare or locally extinct in areas where these critical loads are exceeded. Therefore, the European emission reduction policy is partly based on the critical nitrogen loads for these systems. The differential effects of sulphuric acid and ammonium sulphate deposition on soft-water bodies and their vegetation have been studied in small-scale ecosystems from 1983-1985 (Schuurkes *et al.*, 1987). Following this treatment with artificial acid rain, the chemical and biological recovery of these waters has been determined after a 10-year period.

2. EXPERIMENTAL DESIGN

This study was done in a greenhouse which acted as a shelter for air pollutants. As a consequence, background levels of atmospheric input were negligible (Table 1). Light and temperature conditions resembled the outdoor situation, except for a higher daily maximum during sunny periods. Seven identical small-scale aquatic systems, comparable to ponds, were created in black PEC containers (1.3 x 1.4 x 0.6 m). The sediment was obtained from an undisturbed soft-water lake (pH 6.8; alkalinity 0.7 meq l^{-1}) and consisted of fine mineral sand (0.3 % organic matter), poor in nutrients (N 8; P not detectable; K 18; Ca 5; Mg 17; Fe 25; Na 10 mmol kg^{-1} dry sediment).

Several macrophyte species were introduced in all systems; from oligotrophic soft waters: *Luronium natans*, *Littorella uniflora*, *Myriophyllum alterniflorum* and *Pilularia globulifera*, and from acidified waters *Juncus bulbosus* and *Agrostis canina*. Along the shore *Agrostis canina* was planted together with *Littorella uniflora* and *Juncus bulbosus*. On the terrestrial parts both *Calluna vulgaris* and *Molinia caerulea* were planted. All other species established spontaneously from the seedbank material in the sediment especially *Scirpus setaceus* and *Carex oederi*, both from Nanocyperion communities. This community is characteristic for weakly acidic, temporarily inundated, nutrient poor soils.

From November 1983 to September 1985, each of the systems received ca 500 mm year $^{-1}$ of artificial rain. Besides the control treatment, two major types of rain water were used: water containing sulphuric acid (three levels) and water containing ammonium sulphate (three levels, see Table 1). To study recovery processes, all systems were watered with demineralized water from September 1985 until 1995.

The pH of the water layer was determined monthly with a Metrohm Herisau E-488 pH meter and a combined EA152 pH electrode, during the 2-year experimental period of acid-rain treatment. From May 1990 to 1995 the pH of the water layer was measured monthly with a pHm 82 Standard pH meter. Chemical analysis of the water layer was done during the 2-year period of treatment and once before (September 1994) and after (September 1995) the harvest of the vegetation. Alkalinity was determined by titration of 100 ml water with 0.01 N HCl down to pH 4.2 and acidity by titration of 100 ml water with 0.05 N NaOH to pH 8.2. A part of the samples (100 ml) was filtered through a Whatman GF/C filter (1.2 µm) and, after adding 10 mg citric acid, stored at -20°C for analysis. Ammonium concentrations were colorimetrically determined (Grasshoff and Johanssen, 1977) and Al was measured with an emission spectrofotometer (Jarell Ash Plasma 200, Instrumentation Laboratory). Above ground plant material was harvested in August 1985 and September 1994 and both fresh and dry weights (70°C)

Table 1: pH of the artificial rain water and deposition levels (mol ha^{-1} yr^{-1}) during the period of acid-rain treatment. Bg. = Average background deposition in the greenhouse (after Schuurkes *et al.*, 1987).

Treatment	pH	H^+	NH_4^+	NO_3^-	SO_4^{2-}	PO_4^{3-}	Ca^{2+}	Cl^-	K^+	Mg^{2+}	Na^+
1	5.6	10	80	80	70	2.5	70	395	60	150	285
2	5.0	50	70	220	60	2.5	50	270	40	115	315
3	4.25	250	60	220	230	2.5	60	270	80	185	420
4	3.5	1550	70	220	970	2.5	65	310	100	200	480
5	5.6	10	1380	10	820	2.5	70	460	65	170	320
6	5.6	10	2870	10	1610	2.5	65	430	70	185	330
7	5.6	10	8450	10	4400	2.5	65	440	65	165	320
Bg.	5.6		74	30		19	101	378	42	32	123

quantified. For further details on the experimental design see Schuurkes *et al.* (1987).

3. RESULTS

The recovery of the small-scale soft water systems was studied following a 2-year period of acidic deposition (Schuurkes *et al.*, 1987). In this period it became clear that application of sulphuric acid caused serious acidification of the water layer and led to an increased growth of *Sphagnum* species and *J. bulbosus*, both acid tolerant species. No further changes in species composition were observed. Addition of $(NH_4)_2SO_4$ not only resulted in acidification, but also led to the accumulation of NH_4^+ and SO_4^{2-}. Fast growing species (*J. bulbosus*, *Sphagnum* spp., *M. caerulea* and *A. canina*) outcompeted the characteristic plants in the water layer as well as in the terrestrial parts. At the highest $(NH_4)_2SO_4$ treatment, submerged *L. uniflora* plants disappeared within the 2-year period.

3.1 Chemistry and vegetation during recovery from deposition

Because of the nature of the experiment a gradual increase in vegetation cover is to be expected. In the control system (no. 1), the terrestrial part was gradually colonized by *Molinia* and the aquatic part by two *Sphagnum* spp. Total cover increased to ~ 80% in 1994, with enough space for species of the Littorellion and Nanocyperion communities in all parts of the system (Fig 3 & Table 2). Some introduced plant species (*Luronium*, *Myriophyllum*, *Pilularia*) have disappeared in all systems.

Re-alkalinisation of the water layer occurred within five years after ending H_2SO_4 deposition (systems 2, 3 and 4, Fig. 1 & 2). A slightly enhanced acidity can still be observed in the acid treated systems. This coincides with an increased abundance of acid tolerant species in both the aquatic (*J. bulbosus*) and the terrestrial part (*Hydrocotyle vulgaris*). NH_4^+ concentrations in the water layer of the acid-treated systems have dropped below those of the control system. The total biomass of the systems treated with H_2SO_4 has decreased compared with the control treatment, primarily caused by a reduced growth of *Molinia* and the moss *Polytrichum commune*. In all systems species of the Littorellion and Nanocyperion communities have persisted.

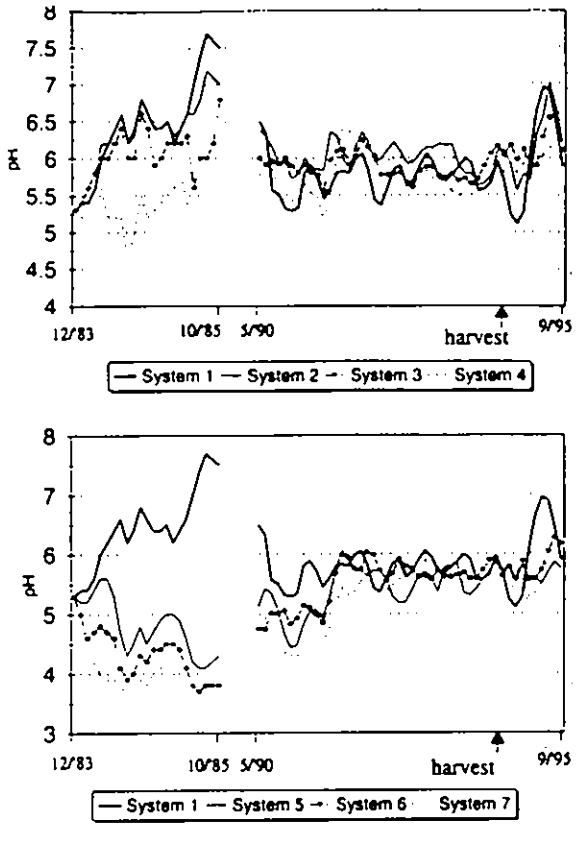

Fig. 1: pH of the waterlayer during the period of application of acidifying rain water and during the period of recovery.

The process of re-alkalinisation is strongly inhibited after $(NH_4)_2SO_4$ treatment (systems 5, 6 and 7). The recovery process of pH takes 6-8 years (Fig. 1). Acidity in the water layer of all systems is slightly enhanced, compared with that in the control system. NH_4^+ and Al levels in the water layer are lower than those found in the control treatment, after ten years of recovery (Fig 2). Despite the recovery in water quality, typical species from oligotrophic conditions have disappeared and fast growing species have become dominant (Table 2).

No re-establishment of acid sensitive species after ending deposition has been observed in any of the systems during the period 1994-1995, except for the establishment of *Pilularia* in the control system in October 1995.

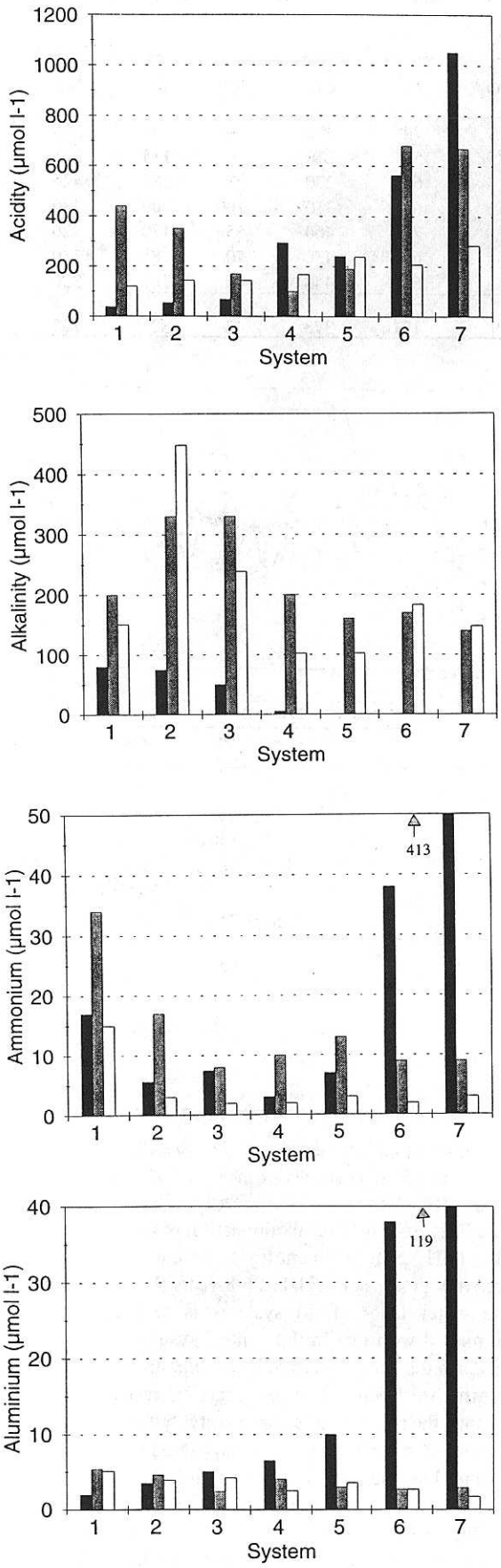

Fig. 2: Water chemistry (acidity, alkalinity, NH_4^+ and Al in µmol l^{-1}) of the small-scale systems at the end of application of acidifying deposition (black), in 1994 (grey) and 1995 (white).

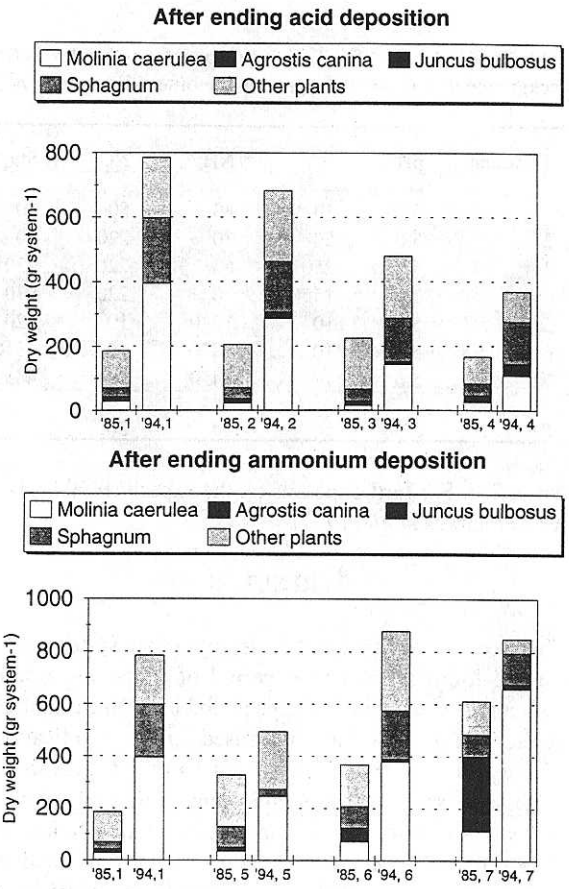

Fig. 3: Above-ground biomass (g dry weight) of the vegetation at the end of the experimental application of acidifying rain water (1985) and after 9 years of recovery (1994).

Table 2: Species composition (g dryweight), total cover and total above-ground biomass of the different small-scale ecosystems in September 1994.

System		1	2	3	4	5	6	7
Total cover (%)		80	75	70	70	90	80	95
Cover 0-20		60	60	60	60	75	55	40
Cover 20-150 cm(%)		25	20	15	15	30	30	60
Cover dead organic matter (%)		7	7	8	8	15	25	50
Total biomass (g dry weight)		785	682	479	370	494	879	851
Acid tolerant species:								
*Molina caerulea**	E	394	285	143	107	244	379	659
Juncus effuses	E	45	68	105	29	95	260	
*Calluna vulgaris**	E	43	46	43	20	24	19	31
Betula spec.	E	0.95						3.7
Juncus squarrosus	E				0.58			
Pohlia nutans	E							0.23
Polytrichum commune	E	65	23	14	2.8	76	7.0	12
*Juncus bulbosus**	E(S)		16	8.6	36	1.8	7.6	3.9
Hydrocotyle vulgaris	E(S)	1.2	0.27	10	8.1	14.6	5.0	8.0
*Agrostic canina**	E(S)	1.3	3.7	0.18	2.8	0.30	4.5	14
Sphagnum denticulatum	E(S)	101	79	72	43	14	19	14
Sphagnum cuspidatum	E(S)	101	79	63	87	11	167	104
Acid intolerant species:								
Osmunda regalis	E	3.3				0.01		
Carex nigra	E	1.5					3.5	
Phragmites australis	E				0.21	11		
Juncus articulatus	E	24	78	17	33	2.0	8.0	
Littorellion species								
*Littorella uniflora**	S(E)	2.0		0.88	0.35			
*Pilularia globulifera**	S		4.9					
Nanocyperiod species								
Carex oederi	E	0.29		1.49	0.52	0.06		
Scirpus setaceus	E	0.68	0.13	0.37	0.08	0.12		

* = Planted species E = Emergent S = Submerged

4. DISCUSSION

Recovery of surface waters from sulphuric acid induced acidification has been reported by several authors (Battarbee *et al.*, 1988, Gunn & Keller, 1990, Wright *et al.*, 1988). In this experiment, pH, alkalinity and chemical ion composition of the water layer returned to pre-acidification levels within 5 years ending H_2SO_4 addition.

Sulphate reduction generates extra alkalinity (Smolders and Roelofs, 1993), as can be observed in the systems treated with H_2SO_4. Although the acidification-induced shift in species composition is still detectable, no severe losses of characteristic Littorellion and Nanocyperion species has occurred. The disappaerance of *L. natans* and *M. alterniflorum* is probably caused by the experimental setup, because of their disappaerance from all systems. The reduced growth of *Molinia* and *Polytrichum* can be a result of a reduced availibility of soil nutrients after sulphuric acid deposition. Furthermore, some root-damage as a consequence of generation of toxic sulfide from the added H_2SO_4 may have contributed to this oligotrophication (Smolders and Roelofs, 1996). Oligotrophication in the water layer occurs in the form of decreased levels of NH_4^+, the dominant N form, possibly caused by a more complete (de)nitrification.

Ammonium-induced acidification has also proven to be reversible, although this process is slower (Fig. 1). Initially plant NH_4^+ uptake is not sufficient to exhaust the accumulated NH_4^+ (Fig. 2). After ending enhanced $(NH_4)_2SO_4$ deposition, re-alkalinisation is probably counteracted by nitrification of NH_4^+, which produces H^+ (van Breemen *et al.*, 1982, Kelly *et al.*, 1982). Oligotrophication processes as observed after ending H_2SO_4 deposition are also found after ending $(NH_4)_2SO_4$ deposition. However, the effects of NH_4^+ enrichment on the vegetation have so far not diminished. After 9 years, the cover of tall plants and the amount of dead biomass increased considerably, compared with the control system. The relative share of *Molinia* in the total biomass increases from 50% in the control treatment to 80% in system 7 (Fig.3). High levels of NH_4^+ deposition overrule the negative effect of acid deposition on total biomass. This has resulted in a decline of species diversity and of the area of open water. Small, prostrate species of mineral soils, belonging to Littorellion and Nanocyperion communities, all disappaered as a consequence of outshading by *Molinia* and the absence of bare soil. The vegetation composition in these systems strongly resembles the present actual vegetation in and along most of the originally oligotrophic, poorly buffered waters in the Netherlands.

It is concluded that oligotrophic, poorly buffered water bodies have a natural capacity to recover after acidification. The recovery of the water quality and vegetation strongly depends on the amount and composition of deposition during the past. $(NH_4)_2SO_4$ deposition causes both eutrophication and severe acidification and has a long term impact on plant species which are sensitive to acid circumstances and to competitive interactions. Considering the N deposition in some parts of Europe ($\pm$ 40 kg N ha^{-1} yr^{-1} in the Netherlands, comparable with that in system 6), it is unlikely that recovery of the vegetation of oligotrophic, soft-waters will occur spontaneously within ten years. Considering the vegetation development after treatment with high concentrations of $(NH_4)_2SO_4$, removal of accumulated biomass after deposition levels have reached critical loads, may prove necessary for restoration. The existence of a restricted natural recovery capacity stresses the urgent need of meeting critical loads for N as soon as possible.

ACKNOWLEDGEMENTS

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AMMONIA FLUXES TO BEECH TREES (*FAGUS SYLVATICA* L.)

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Abstract-Twigs of an about 80 years old beech tree were fumigated with ca. 100 µg $^{15}NH_3$ m^{-3} for 3 days. The flux of atmospheric NH_3 to the twigs showed diurnal variation with highest deposition rates at midday and lowest deposition rates during night. A high correlation between the flux of NH_3 and the transpiration rate was observed. During the day the measured conductance for NH_3 was found to be higher than the NH_3-conductance predicted from the diffusive flux of H_2O. At night predicted and measured fluxes of NH_3 were similar. Determination of the ^{15}N-contents showed that all tissues inside the fumigation chamber were enriched at 10 to 130% in relation to the natural ^{15}N abundance. In addition, an export of ^{15}N from the fumigated part of the twig was indicated by enrichment with ^{15}N of bark and wood of sections of the same twig outside the fumigation chamber. The possible effects of NH_3 uptake on N-metabolism of beech trees will be discussed.

INTRODUCTION

Nitrogen deposition has increased during the last years all over Europe. Efforts to reduce nitrogen emissions have mainly considered nitrogen oxides, whereas the significance of NH_3 as an atmospheric pollutant only recently achieved considerable attention. In Europe atmospheric N trace gases consist at ca. 70% of NH_3 (Diederen & Duyzer, 1988) that is mainly emitted from intensive agriculture (Hadwiger-Fangmeier et al., 1992). Plants are able to take up and metabolise atmospheric NH_3 (Pearson & Stewart, 1993) thereby forcing excess nitrogen influx into plants. As a consequence, nutrient imbalances can be intensified in areas with high nitrogen supply. In close vicinity to the emission source, also direct toxic effects can occur (Hadwiger-Fangmeier et al.; 1992). In the present study we investigated the influence of several climatic parameters on NH_3 flux rates to beech trees in a forest stand. In addition, the fate of atmospheric NH_3 within the beech plants was traced by stable isotope techniques.

METHODS

Experiments were performed with twigs from the sun-crown of ca 80 years old beech trees at the location „Höglwald" in Bavaria (FRG) using the dynamic chamber technique with two identical fumigation chambers of 3 l volume each. In a height of 6 m twigs, still attached to the tree, were enclosed at 20 cm length in one chamber. The other chamber was empty in order to „correct" for chamber specific absorption and desorption. The chambers were fumigated with ^{15}N-NH_3 at a concentration of 100 µg m^{-3}. The airstream of 3 l min^{-1} was controlled by electronic mass flow controllers. A ventilator was installed in the chambers to minimise boundary layer resistance and to allow a rapid mixing of the incoming air. The temperature of the chambers was adapted to the ambient air temperature. Light intensity, air-temperature, relative humidity and concentration of H_2O, CO_2 and NH_3 were determined continuously. The fluxes of NH_3 (JNH_3), H_2O (JH_2O) and CO_2 (JCO_2) were derived from the differences in concentration measured at the outlet ports of the two chambers, the airstream and leaf area as described by Thoene et al. (1991). Fluxes into or onto the leaves are given by negative values. The shoot conductance for NH_3 was calculated as deposition velocity gNH_3 (Thoene et al., 1991). Predicted conductance for NH_3 (pNH_3) was obtained from the water vapour conductance (gH_2O) and ratio of the square roots of the molecular weights of H_2O and NH_3. After fumigation the twigs inside the chamber plus a section of 25 cm outside the chamber were harvested. The plant material was divided into sections and subdivided into leaves, bark and woody tissues. ^{15}N abundance was determined in homogenised samples with a mass spectrometer, ^{15}N enrichment (E%) was calculated as difference between ^{15}N abundance of the sample (A_s) and natural abundance (A_n) in relation to natural abundance.

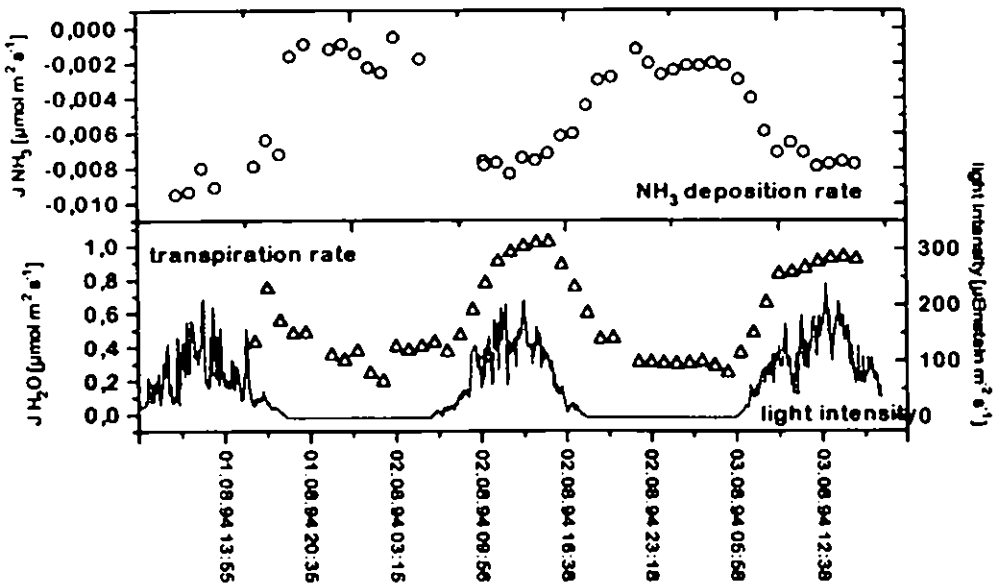

Fig 1: Diurnal courses of H_3 deposition rate (JNH_3), transpiration rate (JH_2O) and light intensity

RESULTS AND DISCUSSION

Diurnal variation of NH_3 fluxes

Fluxes of NH_3 and of H_2O showed diurnal variation (Fig. 1). Highest NH_3 deposition rates of up to -9.5 nmol m^{-2} s^{-1} were found at midday when also the transpiration rate showed the highest values. During night NH_3 deposition rate was much lower with values between -1 and -2 nmol m^{-2} s^{-1}. Because of similar diurnal patterns of transpiration rate and NH_3 deposition rate, there was a high correlation (r^2 = -0.967) between both fluxes (Fig. 2). The correlation between CO_2 flux and NH_3 deposition rate was comparably high (data not shown).

Measured and predicted conductance.

Figure 3 shows the diurnal course of measured and predicted conductance for NH_3 over 24 hours. During night both measured and predicted conductance were in the same range with values of about 0.5 mm s^{-1}. During day predicted conductance (pNH_3) reached values of 2.2 mm s^{-1}, but measured conductance (gNH_3) was up to twice as high. Provided the flux of NH_3 to the leaves occurred only through the stomata, measured conductance for NH_3 should have the same value as the predicted conductance. The quotient (q) of measured and predicted conductance then reaches a value of 1. If the

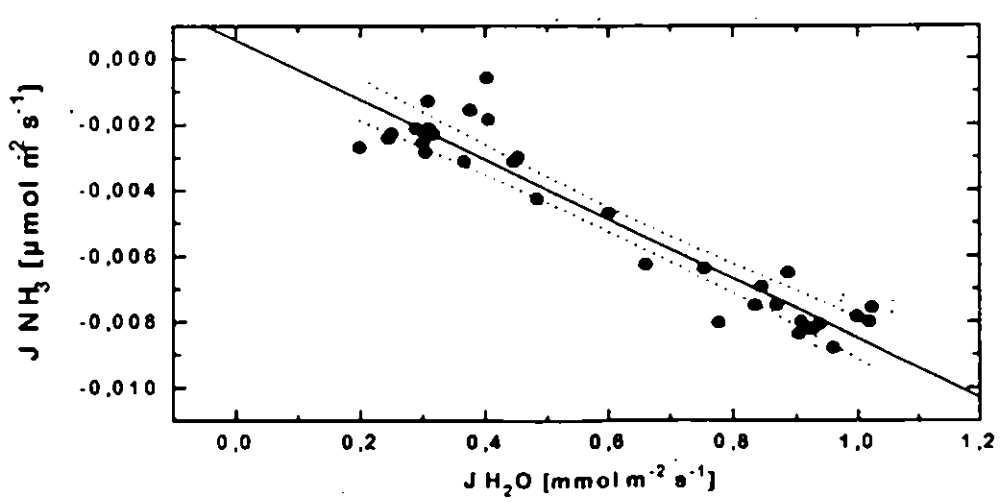

Fig 2: Correlation between the NH3 deposition rate (JNH3) and the transpiration rate (JH2O); regression coefficient amounts to -0.967, confidence limit is 0.95

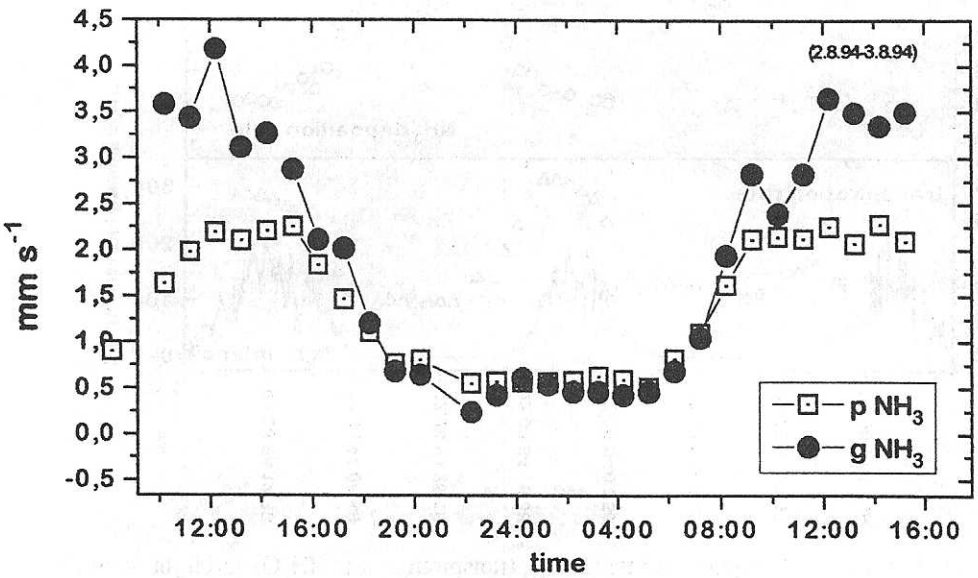

Fig 3: Diurnal course of predicted (pNH_3) and measured (gNH_3) conductance for NH_3

quotient is larger than 1, i.e. measured conductance is higher than predicted, additional factors have influenced deposition. In the present study q showed high correlation with light intensity ($r^2 = 0.804$) and relative air humidity inside the chamber ($r^2 = 0.795$). The dependency of q from air temperature revealed lower significance ($r^2 = 0.571$). Transpiration showed the same diurnal variation as light intensity (Fig. 1). At times of high light intensity transpiration led to an increase of relative air humidity in the chamber with the twig. As NH_3 is highly soluble in water, increased air humidity may have caused the generation of water films on the surfaces of leaves as additional sinks for NH_3 (Burkhardt & Eiden, 1994)

^{15}N-enrichment

The highest rates of ^{15}N enrichment were found in the tissues inside the fumigation chamber (Fig. 4). The values reached from enrichment rates of 129% in the leaves to 11% in the woody tissue. The unfumigated bark and wood outside the chamber also showed a significant ^{15}N enrichment in relation to natural abundance. ^{15}N enrichment decreased with increasing

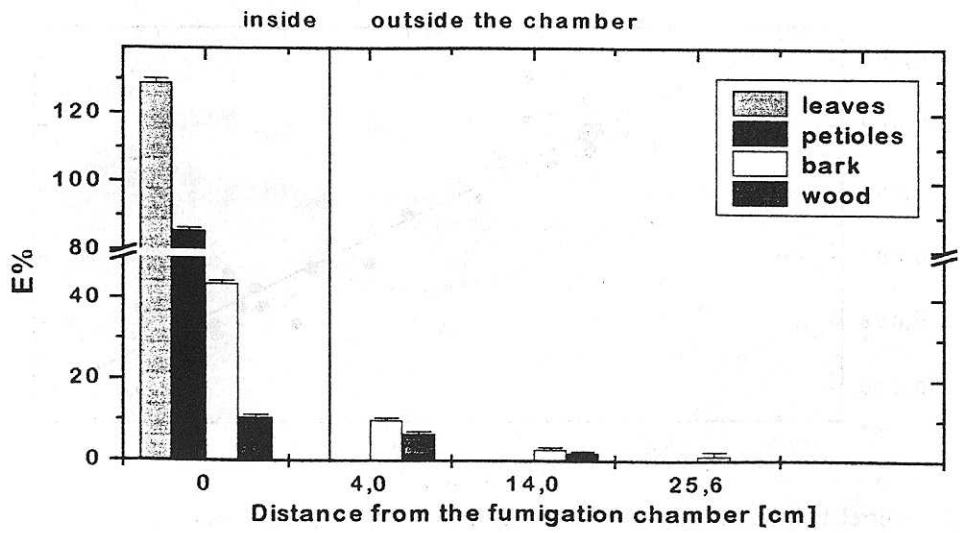

Fig 4: ^{15}N enrichment (E%) of different tissues of the fumigated twig from inside and outside the fumigation chamber

distance from the chamber. The enrichment of the unfumigated tissues is likely to be due to long-distance transport of ^{15}N-compounds from fumigated parts of the plant to sections outside the chamber. Apparently the influx of atmospheric NH_3 is an additional source of nitrogen for the entire tree. The enrichment of bark sections was generally higher than that of wood sections. This finding is consistent with the view that transport of N-compounds from the leaves in direction to the stem takes place via the phloem. ^{15}N enrichment of the wood can be explained by translocation of N-compounds from phloem to the wood where a further transport into the xylem or storage may occur. The daily ^{15}N deposition at 100 µg NH_3 m^{-3} atmospheric concentration to the plant as calculated from the deposition rates found in this study amounts to 116 µg N d^{-1}. The daily deposition calculated from the ^{15}N content in the harvested tissues amounts to 101 µg N d^{-1}, i.e. ca. 87% of the N deposited could be recovered in the plant material. The difference may be due to transport of N-compounds into sections not harvested.

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IS GLUTAMINE SYNTHETASE AN ADEQUATE INDICATOR OF THE EFFECT OF ATMOSPHERIC AMMONIA ON CONIFER TREES?

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Abstract - Glutamine synthetase (GS) is the initial enzyme in the assimilation of NH_3 in higher plants, and is a key factor in the detoxification of NH_3. The potential use of this enzyme as bioindicator is evaluated by reviewing results of own research and recent literature.
At the present state of knowledge GS is unsuitable as indicator for NH_3 effects in the field situation. However, it can be useful in mechanistic studies and sensitivity screenings, which are essential to set standards of NH_3.

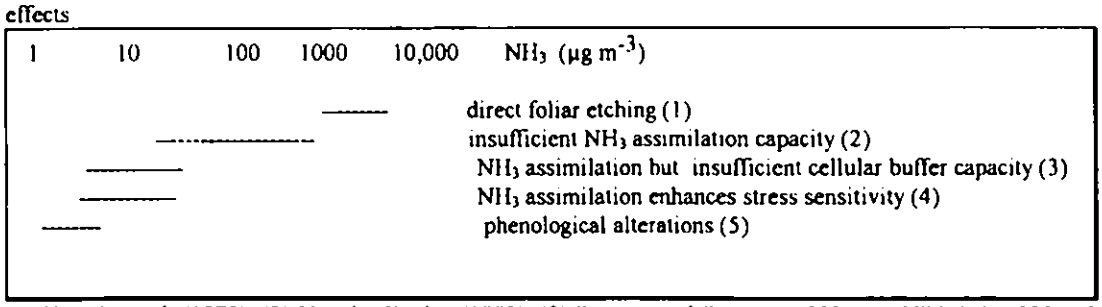
Key words: Glutamine synthetase, ammonia, nitrogen metabolism, bioindicator

INTRODUCTION

The impact of atmospheric NH_3 on plants has recently been reviewed (Fangmeier et al., 1994). This paper focuses in the effects on trees. Detrimental effects of gaseous NH_3 are observed at both low and high concentrations (Fig. 1). Low concentrations act primarily as fertilizer, which in a long term can cause phenological disorders (e.g. reduced generative reproduction, reduced life span), while high concentrations can cause direct damage of foliar tissue (Van der Eerden, 1982 and 1992, Pérez-Soba, 1995). Information on a threshold for toxic effects of NH_3 is useful for field surveys and risk analyses. Glutamine synthetase (GS, EC 6.3.1.2) is the initial enzyme in the assimilation of NH_3 in higher plants (Lea et al., 1992). Quantifying the activity of needle GS may give an early indication of the effect of atmospheric NH_3 on the tree physiology.

The possibility to use GS as indicator was studied in five long-term experiments in which young Scots pine trees (Pinus sylvestris L.) were exposed to gaseous NH_3 and to combinations of gaseous NH_3 with SO_2, with O_3 and with elevated CO_2 concentration. In addition, a field experiment was carried out with mature trees in a region with an estimated N deposition of 40 kg ha^{-1} yr^{-1}. The results of these experiments and recent literature are reviewed in this paper.

Fig 1. Range of NH_3 concentrations hypothesized to be relevant for the different mechanisms leading to adverse effects.



(1) Temple et al. (1979); (2) Van der Eerden (1982); (3) Pearson and Stewart (1993); (4) Nihlgård (1985); (5) Van der Eerden (1992).

EFFECT OF NH_3 ON FOLIAR GS

In fumigation experiments under optimal growth conditions, Scots pine saplings have shown to increase foliar GS activity after exposure to gaseous NH_3 (Pérez-Soba et al., 1994a). The trees responded with enhanced GS activity after exposure to NH_3. Even at high exposure levels (260 µg m^{-3} for 12 weeks) no indication for insufficient GS activity was found. The increase in GS activity might be associated with an increased primary assimilation of NH_3 and with an enhanced reassimilation of photorespiratory NH_3 in the shoots. The increase in GS activity was accompanied by an increase in concentration of N-containing metabolites, such as soluble proteins, leaf pigments and free amino acids. The N derived from gaseous NH_3 was mainly incorporated into

arginine, glutamic acid, aspartic acid and glutamine. In the field experiment, these amino acids, together with proline and histidine, formed the major part of the free amino acid pool in needles mature Scots pine and Douglas fir (Pseudotsuga menziesii (Mirb.) Franco) trees (Pérez-Soba and De Visser, 1994).

FACTORS INFLUENCING GS ACTIVITY

Toxicity of NH_3 occurs when the assimilation capacity of the needles is exceeded. Then, ammonium (NH_4^+) accumulates resulting in physiological and metabolical disorders. Therefore, factors that decrease GS activity, enhance the potential toxicity of NH_3.

Other gaseous air pollutants may induce a decrease in activity of GS in the needles. Fumigation with SO_2 decreased GS activity (Pérez-Soba et al., 1994b), which might be explained by a decrease in the activity of the chloroplastic isoenzyme of GS. Exposure to SO_2 induces a decrease of pH in the chloroplastic stroma (Pfanz and Heber, 1986) and acidity decreases the transferase and biosynthetic activities of GS (Vézina and Margolis, 1990; Bedell et al., 1995). The activity of GS in one-year-old needles also was decreased by exposure to O_3 (Pérez-Soba et al., 1995), which might be due to a decreased reassimilation of N in preference of formation of phenolic complexes, which are deposited in O_3 exposed plants (Jones et al., 1994). In addition, exposure to O_3 may disturb the functioning of the chloroplasts (Lefohn, 1992) and thus, reduce the activity of the chloroplastic isoenzyme of GS.

Climatic factors also may decrease foliar GS activity. Decreases of temperature and light intensity have negative effects on the activity of GS in conifer needles (Margolis et al., 1988; Dueck, pers. commun.).

Some herbicides (e.g. glufosinate and bialaphos) inhibit the activity of GS (Devine et al., 1993; Paton, pers. commun.). These compounds are variations of substituted glutamate and block the incorporation of NH_4^+ into amino acids, which causes an accumulation of NH_4^+ (Vézina et al., 1992).

INDICATORS OF ATMOSPHERIC NH_3 TOXICITY. IS GS AN ADEQUATE INDICATOR?

Gaseous NH_3 is largely absorbed by the shoots (Van Hove et al., 1992) and dissolved in the leaf to form NH_4^+. NH_4^+ in turn is incorporated into glutamine by the action of GS and subsequently incorporated into glutamic acid by glutamate synthase (GOGAT, EC 1.4.1.13 and EC 1.4.7.1). Recent research has confirmed that GS-GOGAT pathway is the major route of the assimilation of NH_4^+ in Scots pine and Norway spruce (Picea abies) (Pérez-Soba et al., 1994a; Aarnes et al., 1995). Following NH_3 assimilation, several parameters have been proposed or used as indicators of susceptibility of conifer trees to atmospheric NH_3. The most used is the N concentration in needles, which gives a very general view of the N status of the plant. It is easy to measure and relations with photosynthesis rate and growth have been described. Recent field surveys in the neighborhood of NH_3 sources indicate that foliar N concentrations of 1.8 to 2.2% are supra-optimal for conifer tree growth (Heinsdorf, 1995). However, long term periods are needed to find significant changes in foliar N concentration of forest trees. Nitrogen may be reallocated from the needles to other tree parts and the stadium of seasonal growth will determine whether the amount of extra N is used for internal cycling or for storage (Millard and Proe, 1992, 1993)

Free amino acids (FAA) show faster and more pronounced changes than N concentration in the needles (Boxman et al., 1995). Arginine (Arg) is particularly important in needles of conifers and has been proposed as indicator of high N deposition (Van Dijk, 1993). Arg seems to be adequate to store N in conditions of excess N, since it has the highest N/C ratio of all the amino acids (4/6). However, changes in its foliar concentration are not only associated with N overload. In literature, changes in Arg concentration in needles have been related to modification of the nutrient balance or variations in the water relations, which are affected by high N availability as well (Van Dijk and Roelofs, 1988; Näsholm and Ericsson, 1990; Vance and Zaerr, 1990). Recent research shows that Arg plays also an important role in the transport of N in the stem, additional to its role as N-storage (Aarnes et al., 1995). In addition, soluble amino acids show diurnal and seasonal changes which, in turn, vary strongly over the years (Pietiläinen and Lähdesmäki, 1986; Manderscheid and Jäger, 1993).

NH_4^+ concentration in needles is considered the most direct indicator of NH_3 toxicity, since it needs to be assimilated to avoid metabolical disorders (Monselise and Kost, 1993). Its measurement using in vivo NMR spectroscopy gives quantitative and qualitative data during the course of N assimilation and informs about the distribution of NH_4^+ between cytoplasm and vacuole (Aarnes et al., 1995). NMR is very adequate for laboratory experiments but its use for the field situation is complex. In addition, conifers show a high capacity to store high concentrations of NH_4^+ in vacuoles of roots, needles and even stems (Aarnes et al., 1995).

Comparison of ratios FAA pool/total N and free NH_4^+/total N has been proposed as indication of NH_3 assimilation (Pérez-Soba et al., 1994a) NH_3 assimilation will be indicated by a high FAA/total N ratio, while deficient assimilation will be indicated by a high free NH_4^+/total N.

The activity of GS is a primary factor in NH_3 assimilation and plays a major role in lowering the levels of NH_4^+ in the cytoplasm. However GS is not an adequate indicator of NH_3 toxicity for conifer trees for several reasons. Firstly, the assimilation of NH_3 itself may lead to adverse effects if the release of H^+ in the cytoplasm exceeds the buffering capacity (Pearson and Stewart, 1993) or if the stress sensitivity is enhanced due to N excess (De Kam et al., 1991; Dueck et al., 1991; Heinsdorf, 1995). Secondly, its activity shows significant diurnal and seasonal variations (Pérez-Soba and De Visser, 1994), which are difficult to explain in field surveys

CONCLUSION

At the present state of knowledge, GS is an unsuitable indicator for NH_3 effects in the field situation. However, it can be useful in mechanistic studies and sensitivity screenings, which are essential to set standards for atmospheric NH_3.

In mechanistic studies, more research is needed on GS. It is known that GS activity in shoots of conifer trees is generally high enough to assimilate NH_3, even at concentrations representative for regions with intensive livestock farming. However, interactions of GS with factors decreasing its activity have not yet been quantified, and thus situations in which GS is inhibited to a degree that NH_4^+ causes toxic effects are not yet taken in account. In addition, there are few studies on the cytoplasmic and chloroplastic isoenzymes of GS in conifers, and particularly in response to NH_3. The two isoenzymes strongly vary between cell types and plant species, and may react differently to changes in cellular pH due to its location in the cell. The role of GS in the control of root N uptake by shoot N uptake should be investigated, since the in vivo prevention of nitrate assimilation by NH_4^+ and glutamine may require the presence of the active form of GS, as suggested for cyanobateria (Tapia et al., 1995).

In sensitivity screenings, differences in susceptibility of tree species to atmospheric NH_3 may be assessed as differences in GS activity in the needles, which indicate a difference in capacity to assimilate high concentrations of atmospheric NH_3 (Pérez-Soba and De Visser, 1994).

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ABSTRACTS

AUGIAS: A DECISION SUPPORT TOOL FOR REGIONAL AMMONIA AND MANURE PROBLEMS

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Intensive stock breeding in the Netherlands is responsible for a substantial share of GNP. As a consequence the size of the activities has caused a number of different environmental problems of which eutrophication of nature and impaired drink water stocks are the more serious ones. In addition, ammonia emissions from manure are a major cause of acidification in the Netherlands.

Since the late eighties a manure and ammonia policy is being developed. Up till now, most measures resulting from this policy do not seem to reflect the integrated approach based on environmental benefits and cost-effectiveness. Also, though the problem is primarily one of regional scale, the potential of the regional approach has not been fully exploited. As a further consequence systematic monitoring of the progress in the implementation of policy measures is hardly possible.

In order to address these problems properly, TNO developed the model AUGIAS. With this model the manure and ammonia problem is approached in an integrated way leading to insight in environmental benefits and costs of different measures. The model offers the option to present a complete picture of the nitrogen balance in the intensive stock breeding system, which implies that the progress as a result from policy measures may be monitored. Furthermore, the model provides an insight in a regional situation and the need and options for a region-oriented approach.

The structure and options of the model are based on an analysis of the intensive stock breeding system. Results from a number of studies have been carried out in the Netherlands. The role of the model as a tool for obtaining scientific consensus on a complex environmental problem, with important economic consequence has been assessed with a view on future research.

EXPERIMENTS ON THE IMPORTANCE OF DIFFERENT FACTORS INFLUENCING AMMONIA EMISSIONS FROM ANIMAL HOUSES

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To provide information about the importance of different factors of ammonia emission in animal houses and during manure storage, emission experiments with cattle excrements were done under controlled conditions in respiration chambers. Different types of slurry and solid manure were mixed from fresh cow urine and dung. While these manures were exposed in the chambers for three to four days, ammonia in the exhaust air was monitored. The factors temperature, air exchange rate and emitting surface were changed one at a time in various steps. Thus the influence of these factors and of manure content can be assessed with regression analysis. For example, it could be shown that under the conditions studied emissions from solid and liquid manure have the same dependance on ammonia content. The data from these experiments should also provide the basis for an empirical model to estimate emissions from animal houses.

A MODEL OF AMMONIA VOLATILIZATION FROM A GRAZING LIVESTOCK FARM

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A dynamic model was developed to predict the ammonia volatilization from grazing livestock farms and to allow potential control measures to be evaluated. The relationships within the model were based on the underlying physical and chemical processes, but empirically based factors were used to reduce the demand for input data and where the understanding of the underlying processes was inadequate. On a daily basis, the model simulates the partitioning of dietary nitrogen into dung and urine and its subsequent fate within the pasture or the slurry handling system. The fate of dry matter and water added in dung, urine and from other sources is also predicted. The model illustrates the indirect interactions between ammonia sources, highlights the influence of slurry management on ammonia losses, stresses the need for integrated, whole farm measurements and demonstrates that assessments of the impact of control measures may be misleading unless considered at the scale of the whole farm.

AMMONIA EMISSIONS AFTER APPLICATION OF LIQUID MANURE ON GRASSLAND

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In those regions of Europe dominated by cattle management, a considerable proportion of liquid manure is used as a permanent grassland fertilizer. However, the all-year-long plant cover on grassland forms a strong obstacle for emission reduced soil infiltration of liquid manure when using standard application techniques.

In the framework of a research project entitled "Ammonia Emissions After Liquid Manure application on Grassland", normal agricultural practice oriented outdoor experiments were carried out in combination with investigations under controlled conditions (i.e. temperature, relative humidity, wind velocity). For the latter, wind tunnel and microplot measuring units were employed which made a variance analytical evaluation of the experimental data possible.

Objectives:

- Quantification of the influence of the climatic factors *temperature wind, velocity* and *rainfall* on ammonia emissions by employing various application techniques
- Determination of the influencing factors *soil, plant cover density* and *dry matter content of the liquid manure* and their interactions on ammonia emissions by employing various application techniques

By applying the results of the investigations under controlled conditions it is possible to interpret the results from the agricultural practice oriented outdoor experiments with respect to ammonia loss and rate of ammonia loss after an application of liquid manure.

INTERCOMPARISON OF FIVE METHODS FOR MEASURING AMBIENT AMMONIUM AEROSOL CONCENTRATIONS

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In the Netherlands National Air Quality Monitoring Network, hourly average NH_3 and daily average NH_4^+ concentrations are measured at eight sites on a continuous basis. The NH_4^+ concentrations are measured with a Low Volume Sampler (LVS), consisting of a denuder filled with active charcoal for removal of reactive gases followed by a Whatman 42 filter to catch the aerosols in the sampled air (flow rate: 1.8 l min^{-1}). Since there was some doubt about the reliability of the method, it was studied in our laboratory, together with four other methods: two alternative LVSs (one with a citric-acid impregnated filter and one with a citric-acid impregnated backup filter), a three-stage filter pack and an annular denuder system (ADS).

Ammonium sulphate and ammonium nitrate aerosols as well as gaseous NH_3 in various concentrations were supplied to the instruments via a manifold at 50% r.h. and 20°C. During some experiments, NH_3 was mixed with one of the generated aerosols to study effects of the NH_3 - NH_4^+ equilibrium on the measurements. Further, effects of r.h. were studied by varying r.h. in the manifold at constant aerosol concentration. The size distribution of the supplied aerosol was determined with a TSI Scanning Mobility Particle Sizer. As a check, the aerosol concentration was determined by sampling air from the manifold over a Teflon filter. An ECN continuous-flow denuder was used to measure the NH_3 concentration in the manifold. During all the experiments, the sampling time was approximately 2.5 h. Concentrations were chosen in such a way that the amounts of NH_4^+ sampled by the methods corresponded to daily concentrations in ambient air. After sampling, filters and denuders were extracted and analysed for NH_4^+ by the detector unit of the continuous-flow denuder. Some samples were also analysed on sulphate or nitrate, using Ion Chromatography.

At this time, only the experiments with ammonium sulphate and NH_3 have been performed. Preliminary results show that the ADS gives systematically higher values for the ammonium sulphate concentration than the other methods. For the LVS, this might be explained by loss of particles in the active charcoal denuder. The Whatman 40 filter of the filter pack probably does not catch all the particles. In an additional experiment, the particle concentration behind the filter was measured with a Condensation Nucleus Counter. This showed that 10-20% of the particles passed the filter. No significant dependence on relative humidity was found for all the methods studied. The NH_3 concentrations measured by the filter pack and the ADS agreed with the concentration in the manifold. The ammonium nitrate experiments have not been finished yet.

EFFECTS OF SAMPLING TUBE ON MEASUREMENTS OF AMMONIA CONCENTRATIONS IN AMBIENT AIR

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In the Netherlands National Air Quality Monitoring Network (NAQMN), hourly average NH_3 concentrations are measured with ECN continuous-flow denuders. Each of these instruments is installed inside a container and the air is sampled from approximately 1 m above the roof of the container via a sampling tube to the instrument. Since NH_3 is known to absorb very well to several materials, we studied the effect of several 'tube parameters' on the measured concentration. The parameters studied were tube material (FEP Teflon and polythene), tube length (2 and 10 m), and 'rate of pollution'. For the latter experiment, 20 and 80 m^3 of ambient air had been sucked through several tubes, which were further denoted as 'polluted' and 'highly polluted'. Clean tubes were studied as well. In addition, a 1.3-m long ('not polluted') stainless steel tube was tested. The experiments were carried out in an environmental test chamber, where ca. 40 $\mu g\ m^{-3}$ NH_3 and clean air (from two separate manifolds) were alternatively supplied to two ECN continuous-flow denuders, one via a 0.5-m long FEP Teflon reference tube and the other via one of the tubes to be studied. The flow rate of the continuous-flow denuders was 4 l min^{-1}. The response times and final concentrations (after completion of the step change) were determined for both instruments. Experiments were conducted with both dry and humified air (50% r.h.).

In all the experiments, the supplied and measured NH_3 concentrations after complete step change agreed within 2%, showing that no NH_3 was lost during transport through the sampling tubes. However, the response times differed. For the step NH-zero air, nearly all the tubes including the reference showed response times (95% change of concentration) of 6-10 min for dry air and 10-15 min for humified air. For the reverse step, response times were generally 9-13 min for dry air and 15-20 min for humified air. Only the 10-m FEP Teflon tubes, especially the polluted ones, and the RVS tube showed higher values, up to 20 min for the step NH-zero air and 33 (FEP) to 40 (RVS) min for the reverse step. For most of the tubes, effects of pollution and length were hardly detectable, although on average the shortest response times were found for the unpolluted and shortest tubes. From the results polythene was selected as the best material for the sampling tube in the NAQMN.

In addition, NH_3 concentrations were measured for a few months at one of the NAQMN sites using two continuous-flow denuders both sampling at their 'normal' flow rates (30 l min^{-1}), one via a 2-m long, 9-mm i.d. polythene tube and the other via the stainless steel common sampling inlet used in the NAQMN. The latter instrument reacted slower on rapid concentration variations and peaks were attenuated and broadened. Hence, the stainless steel common sampling inlet is not appropriate for the NAQMN. These results agree with those of the laboratory study.

THE ROLE OF OCEANIC NH_3 EMISSIONS ON GLOBAL ABUNDANCES OF ATMOSPHERIC AMMONIA AND AMMONIUM COMPUTED WITH A 3D CHEMISTRY-TRANSPORT MODEL OF THE TROPOSPHERE

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One of the major uncertainties in the global ammonia budget is emission from the oceans. Previous estimates of oceanic emissions ranged from virtually zero to more than 20 Tg N yr^{-1}, the latter being a major fraction of the total ammonia emissions (45-75 Tg N yr^{-1}). In the present work we use a global 4-5 degree 19 layers atmospheric transport model TM2/TMK, to investigate the role of oceanic NH_3 emissions on the transport and chemistry of NH_3 and NH_4^+ in the marine atmosphere. Deposition and emission of NH_3 is calculated using oceanic NH_4 concentrations calculated with a global oceanic circulation model and piston velocities calculated from the windspeed and stability. A comparison of model results with measurement of NH_3, NH_4^+ and wet deposition of NH_4 in remote and coastal marine regions has been made and uncertainties assessed.

THE SENSITIVITY OF AEROSOL AMMONIUM DEPOSITION TO THE UNCERTAINTY IN AMMONIA EMISSIONS OVER EASTERN NORTH AMERICA: A MODELLING STUDY

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The behaviour of ammonia over eastern North America is strongly affected by the spatial incoherence of the patterns of ammonia emissions and sulphur emissions. Further, the uncertainty in the ammonia emissions is estimated to be as much as a factor of 5 (Chang *et al.*, 1990). There is also evidence that this uncertainty itself may have a spatial pattern (McHendry and Dennis, 1994) Results from a modelling study using the Regional Particulate model, a three-dimensional Eulerian air quality model which includes aerosol processes (growth, coagulation, nucleation, etc) show how the wet and dry deposition of total ammonia and the dry deposition of gaseous ammonia and aerosol ammonium are related to various estimates of uncertainty in ammonia emissions.

Chang, J.S. *et al.* (1990), The regional acid deposition model and engineering model, State of Science/Tech Report No 4, National Acid Precipitation assessment Programme.
McHendry, J.N. and Dennis, R.L. (1994), *J. App. Meteor.*, Vol 33, pp 890-905.

SURFACE EXCHANGE OF AMMONIA OVER GRAZED PASTURE: A CONTRIBUTION TO THE EUROTRAC SUBPROJECT BIATEX

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Continuous measurements of the atmosphere/surface exchange of ammonia over grazed pasture have been carried out from July 1992 until July 1994 at Zegveld, in a peat soil region in the central western part of the Netherlands. According to the gradient method, fluxes were measured over the terrains of a research centre for dairy cattle farming. Farm type and management were highly representative for agriculture on fenn grassland, which constitutes about one third of the total grassland area in the Netherlands.

The availability of detailed documentation of the treatments of the terrains allowed a study of their impact on ammonia exchange, in addition to influences of other surface conditions, of meteorology and of other airborne pollutants such as sulphur-dioxide and ammonium-nitrate.

The work has attempted to account for all of these conditions on diurnal and/or seasonal scale in a parameterization of ammonia exchange over grazed pasture, Eventual consequences for transport models of ammonia have also been evaluated.

MODELLING THE DRY DEPOSITION OF AMMONIA, NITRIC ACID, AND AMMONIUM NITRATE

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Numerical investigations regarding the exchange of HNO_3, NH_3 and NH_4NO_3 between the atmosphere and the biosphere have been made. The investigations were performed with a modified inferential method which is based on the generally accepted micrometeorological ideas of the transfer of momentum, sensible heat and matter near the Earth's surface and a possible chemical interrelation among these nitrogen compounds. This modified inferential method calculates the micrometeorological quantities (such as the friction velocity and the fluxes of sensible and latent heat), the height-invariant fluxes of the composed chemically conservative trace species with 'group' concentrations $c_1 = [HNO_3] + [NH_4NO_3]$ (total nitrate), $c_2 = [NH_3] + [NH_4NO_3]$ (total ammonia), and $c_3 = [HNO_3] + [NH_3]$, as well as the fluxes of the 'individual' nitrogen compounds. The parameteriSation of the fluxes is based on the flux-gradient relationships in the turbulent region of the atmospheric surface layer.

The model results show that the dry deposition fluxes of these trace constituents may be strongly affected by chemical interrelation. These results differ considerably from those derived with the constant flux approximation, sometimes of up to several hundred percent.

MEASUREMENTS OF AMMONIA FLUXES AND DRY DEPOSITION VELOCITIES TO A SPRUCE FOREST IN DENMARK

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The fluxes of ammonia as well as the dry deposition velocities have been estimated from measurements of the gradient above a Spruce forest in the western part of Denmark. The air concentration measurements were done by denuders at the heights of 18, 24 and 36 m. The canopy is about 12 m tall. Measurements have been performed in six periods of about 8-10 days, at different times of the seasons. The dry deposition velocities ranged from relative high values, apparently limited by the aerodynamic resistance only, with little or no surface resistance, to negative values indicative of emission. About one third of the measurements show emission profiles. In a period with low ammonia concentrations, measurements at the forest floor and in the middle of the canopy corroborate that emissions from the forest takes place. In a warm period with high ammonia concentrations the measured net flux also show emission.

TRANSFER OF NH_X COMPOUNDS BETWEEN THE ATMOSPHERE AND A FOREST

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The development of forest ecosystems depends to a large degree on the nitrogen compounds available for biological activity. These nitrogen compounds can be supplied from an internal turnover of biomass and/or from the external input from the atmosphere. The nitrogen transfer as gaseous NH_3 and as ionic ammonium at an old spruce forest has been quantified on the basis of field measurements of particle deposition, NH_3 mass balance in branch enclosures, rainfall, throughfall, fog deposition and NH_3 concentrations. The main NH_4-NH_3 fluxes into this forest seem to be precipitation and particle deposition. Gaseous NH_3 exchange is most uncertain. Reduced nitrogen input is of the same order as oxidised nitrogen input, so that the nitrogen supply from the atmosphere to this forest ecosystem seems to be far to much in comparison to the need for the growth of the tree stand.

INFLUENCE OF LEAF TEMPERATURE AND TRANSPIRATION OF PLANT-ATMOSPHERE AMMONIA EXCHANGE

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Transpiration was shown to play an important role in the regulation of NH_3 emission between plants and the atmosphere. Different transpiration rates were obtained by changing the leaf temperature, light intensity and air humidity, respectively. At increasing light intensity (0 - 600 μmol m^{-2} s^{-1}) and decreasing (10-95% RH) a significant linear increase in NH_3 emission was observed, being dependent on the nitrogen level of the plants. This linear response could solely be ascribed to changes in stomatal conductivity. However, at increasing leaf temperatures (10 - 40°C) an exponential rise in NH_3 emission was found, indicating that an increase in stomatal conductivity not alone could explain the observation. It was demonstrated that the NH_3 compensation point, calculated on basis of apoplastic pH and NH_4^+ concentration, was an important factor in the regulation of NH_3 emission from plants at increased temperatures. Using various thermodynamic equations to correct for temperature effects on the gas-liquid phase equilibria for NH_3 and NH_4^+ and using transpiration data, the effect of increasing temperatures on NH_3 emission, could be predicted with a high accuracy.

PLANT-ATMOSPHERE NH_3 EXCHANGE IN RELATION TO GLUTAMINE SYNTHETASE ACTIVITY AND N UPTAKE BY ROOTS

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Barley (*Hordeum vulgare* L. cv Golf) was grown in solution culture with controlled nitrogen availability. Ammonia emission measured in cuvettes connected to an automatic NH_3 monitor was close to zero for plants supplied with nitrate and was not affected by the previous growth on two different relative addition rates of nitrate-N; 0.1 and 0.2 day^{-1}. Ammonia emission increased to 0.88 nmol NH_3 m^{-2} s^{-1} for plants transferred to a growth medium with 2 mM ammonium.. Inhibition of glutamine synthesase (GS) by 0.5 mM methionine sulfoximine (MSO) caused the total extractable GS activity in both shoots and roots to decrease dramatically. At the same time ammonia emission increased and after 24 h reached ca. 50 nmol NH_3 m^{-2} s^{-1} in both NO_3^- and NH_4^+ grown plants.

Ammonia emission was also measured on wild-type and mutant plants of barley (cv. Maris Mink), which had only 47 to 63% of the chloroplastic glutamine synthesase activity. Mutants showed increased ammonia emission compared to wild-type plants. The 63% GS mutant usually showed higher ammonia emission than the 47% GS mutant. This agrees with higher ammonium and lower amino acid contents found for 65% GS mutants compared to mutants with less than 65% GS activity (Häusler *et al.*, 1994) and suggests an inhibition of ammonium release in plants with very low GS activity. Ammonia emission of the mutants was also more affected by increasing leaf temperatures and light intensity compared to wild type plants, indicating that the mutants were more sensitive to increased photorespiration.

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RESPONSE OF A SPRUCE FOREST ECOSYSTEM TO STRONG AMMONIUM INPUT REDUCTION IN A "CLEAN RAIN" ROOF EXPERIMENT

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In the Solling experimental forest in central Germany a 'clean rain' roof manipulation study is run in a 60 year old Norway spruce (*Picea abies* Karst.) stand.

Sprinkling water applied underneath the 300 m^2 roof contains no ammonium, whereas the ambient throughfall at the site has an average concentration of ca. 210 μmol/l. Besides of ammonium, nitrate and sulfate input fluxes to the soil are strongly reduced (reductions of ca. 90 and 85% compared to ambient flux, respectively).

The response of soil solution chemistry to reduced input of N and S was strong and rapid. Ammonium concentrations decreased below detection limit in the upper mineral soil water samples after 0.5 y of clean rain treatment and have remained there ever since.

The fine roots of the spruce trees reacted strongly to the changes in soil water chemistry. Living fine root biomass increased in the clean rain plot by ca. 40% compared to pre-experimental conditions.

The results demonstrate that:

in spruce forests on acid soil atmospheric element input largely controls soil solution chemistry and that

strict air pollution control measures would have a significant and quite rapid effect with respect to ameliorating soil water chemistry, acid stress and forest vitality.

EFFECTS OF AMMONIUM SULPHATE ON NUTRIENT STATUS, CANOPY LEACHING AND DROUGHT RESISTANCE OF NORWAY SPRUCE

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A laboratory experiment was set up to study effects of ammonium on nutritional status of two-year-old Norway spruce (*Picea abies*) plants. The treatments were given as artificial rain to the canopy with the plant roots and soil isolated from the spray solution. Three treatments were used: control (C) (plants treated with demineralised water), acid rain containing sulphur (S) (H_2SO_4, pH 4.0); or acid rain containing ammonium sulphate (N) ($(NH_4)_2SO_4$, pH 4.0). The plants were sprayed twice a day, five days a week during 35 days. Throughfall was collected for analysis after each treatment. Biomass samples were taken out on four occasions and nutrients in the needles were analysed. Later the plants were exposed to drought for 14 days; rewetted, and the vitality of the plants was recorded. There was a net uptake of nitrogen in the canopy of plants in the N treatment concomitant with a net efflux of base cations leaching from the needles. These plants leached approximately twice as much as the plants in the S treatments and four times as much as the control. However nutrient concentrations in the needles remained unchanged. No significant effects of the N-application was found for above ground biomass, possibly due to self thinning causing a large variation between individuals. However, the drought resistance was severely affected in plants receiving the S treatment and even more so in plants receiving the N treatment.

NITROGEN DEPOSITION - EFFECT ON NUTRIENT IMBALANCES AND WATER RELATIONS OF FOREST TREES

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Bulk deposition and throughfall measurements across Switzerland revealed that N deposition exceed critical load values of the UN-ECE (1992) guidelines for forests in most forest areas except in altitudes >1500 m asl. In permanent observation plots - 64 sites all over Switzerland - the nitrogen supply of beech and Norway spruce increased significantly in the past ten years whereas phosphorus (beech and spruce), potassium (spruce) and magnesium (beech) decreased. About all, the ratios of nutrients changed, hence increasing nutrient imbalances. Field data suggest as well that there is a correlation between nitrogen deposition and increased N/P ratio in leaves.

In an experimental study it could be shown that applications of 25-50 kg N ha^{-1} yr^{-1} decreased P, K and Mg supply and enhance N/P, N/K and N/Mg ratios significantly in potted beech and spruce after 2 and 5 years respectively. After 8 years, 100 kg N ha^{-1} yr^{-1} caused slight symptoms and 200-400 kg N ha^{-1} yr^{-1} acute damages due to nutrient disturbances about all in spruce. N-applications of ≥25 kg N ha^{-1} yr^{-1} increased the shoot:root ratio and leaf biomass significantly, leading to increased water stress susceptibility as it was observed in a drought experiment

EFFECTS OF AMMONIA ON FOREST GROUND FLORA IN THE VICINITY OF A POULTRY FARM

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Atmospheric ammonia is recognised as an important atmospheric pollutant that may result in both acidification and eutrophication of ecosystems. Changes in species composition associated with increased N deposition, and particularly with NH_3 emissions from intensive agriculture, have occurred over much of Europe. Agricultural sources of NH_3 such as intensive animal units or farmyard manure stores are situated in the countryside frequently in close proximity to woodlands and heathlands. Some of these habitats will be of conservation interest and protected as Sites of Special Scientific Interest or even National Nature Reserves. A study has been made of the dispersion and effects of ammonia from a poultry farm in southern Scotland surrounded by fairly open fern-rich coniferous woodland. The farm contains 120,000 broilers and is situated in an area of low density mixed agricultural, with a background ammonia concentration of 1 ppb. Ammonia concentrations were large close to the poultry houses (long term mean of 13 ppb and 3-weekly ranges of up to 35 ppb at the down-wind site, 16 m north of the poultry unit wall, at the wood boundary) and declined exponentially, reaching half the wood edge value at 20 m into the forest and approaching background upwind values at 300 m in the forest.

Species composition of the forest ground flora was adversely affected within 50 m of the emission source with a 20% decline in species number and an increase in species such as *Chamaenerion angustifolium Deschampsia flexuosa* and *Holcus lanatus*. Nitrogen content in foliage of pleurocarpous moss species was very large (3%) close to the unit, declining to the upwind concentration at about 300 m from the poultry unit. Using the relationship previously described between bryophyte tissue and atmospheric nitrogen deposition (Pitcairn *et al.*, 1995), nitrogen deposition to the woodland surrounding the unit was estimated to be in the region of 100 kg N ha^{-1} yr^{-1}, not too disimilar from the value estimated from wet deposition of NH_4^+ + NO_3^- and dry deposition of NH_3 and NO_2 of 78 kg N ha^{-1} yr^{-1} based on air concentration and deposition velocities. Nitrogen deposition at this site is very large and exceeds recommended critical loads for acidic coniferous forest i.e. 15-20 kg N ha^{-1} yr^{-1} to protect ground flora and is also in excess of that (11->50 kg N ha^{-1} yr^{-1}) proposed to protect tree health (Hornung *et al.*, 1995). Critical levels of ammonia proposed at Egham (11.6 ppb annual mean; Ashmore & Wilson, 1994) are also exceeded at the woodland edge and it is probable that the damage observed on spruce and pine (needle yellowing and needle loss) at the poultry farm may be due both to high concentrations of ammonia and N deposition. Although changes in species composition were confined largely to the immediate 50 m, foliar nitrogen content was affected for a distance of 300 m . Variations in soil type and light intensity may play a role in the changes observed. Experiments to further investigate these effects are in progress together with studies centred around other animal units.

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EFFECTS OF AMMONIUM SULPHATE DEPOSITION ON A LOWLAND DRY HEATH

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Critical loads of nitrogen are currently based on computer models which predict that long-term nitrogen deposition will lead to increased tissue nitrogen levels; these will be accompanied by increased sensitivity to secondary stresses which may in turn lead to canopy breakdown and replacement by acid grassland communities. However, there is a lack of empirical data from long-term experiments at deposition rates close to the proposed critical load of 15-22 kg N ha^{-1} yr^{-1} to validate model-based predictions.

Since 1989, the effects of adding 7.5 kg N ha^{-1} yr^{-1} or 15.4 kg ha^{-1} yr^{-1}, in the form of ammonium sulphate, to a lowland dry heath have been investigated to Thursley Common, a National Nature Reserve, located about 45km SW of London. The background deposition at this site is approximately 15 kg ha^{-1} yr^{-1}, close to the proposed critical load.

Over the past five years, there have been large and significant increases in shoot growth, flowering, canopy density and litter production of heather in response to the nitrogen additions. However, only small, non-significant increases in shoot nitrogen content have been observed, with no clear evidence of altered sensitivity to biotic or abiotic stresses. Nevertheless, some of the responses observed suggest the potential for increases in heather beetle attack, late spring frost damage, and possibly plant water stress. Thus the experimental results at this stage offer some empirical support for the proposed critical load value.

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Atmospheric Ammonia: Poster Proceedings

The emission, behaviour and fate of atmospheric ammonia is increasingly being recognized as a major issue in assessing and minimizing the impact of atmospheric pollutants. In addition to sulphur dioxide and nitrogen oxides, which originate from large combustion and transport sources, ammonia, mostly arising from agiculture, represents a substantial contribution to acidifying pollutant emissions. Coupled with this is the contribution of ammonia deposition to nitrogen eutrophication of ecoystems, as well as its importance, though atmospheric chemistry, in modifying the budgets of other pollutant gases. An appreciation of each of these effects has led to a large increase in the scientific attention given to the behaviour of ammonia.

A key impetus to the science has been the need to underpin policy considerations to minimize acidifying and nitrogen deposition. Particularly within the UNECE Convention on the Long-Range Transport of Air Pollutants, discussions have now moved to update the exisiting 'NO_x Protocol' to consider both NO_x and ammonia emissions and measures to reduce them. With this in mind the UK Department of Environment sponsored this International Conference on Atmospheric Ammonia. The aim was to draw together the international scientific community and assess the current state of knowledge on the complete atmospheric cycle, fate and current control strategies of ammonia. The proceedings are published in two parts, as a special issue of *Atmospheric Environment* and the present volume, which reports results from the large number of poster presentations made at the conference.

Cover: Oilseed rape field near North Berwick, Scotland. Site of a joint field measurement campaign of the EC project 'Exchange of Atmospheric Ammonia with European Ecosystems' (EXAMINE), June 1995.